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Effects of organic and inorganic fertilizers in northeast Asian agriculture – a case study in Hokkaido and Mongolia –

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Contents

Chapter I. Introduction: Problems of fertilizer use in the world

Fertilizer is added to soil to make the soil more nutritious for plants. In agriculture, fertilizer comes from organic sources, such as manure, or manufactured chemically. Generally, most fertilizers contain one or more of nutrients such as nitrogen, phosphorus or potassium, since these ingredients are the most important nutrients for plant growth. In particular, fertilizers replenish the nutrients removed from soils by harvested crops, and encouraging adoption of high-yielding and increase biomass in the nutrient-poor soils.

In the world, chemical fertilizer use in the 1960s was 27.4 million tons, and was increased in 1990s to 143.6 million tons. Furthermore in 2015, it is estimated to reach to 190.0 tons (Heffer et al., 2012). Chemical fertilizer use increased in both developed and developing countries, but the annual increase rate of fertilizer use in developing countries recorded substantially higher raise (10.5 million t/year), albeit from a small, their share of global fertilizer consumption has increased from 10 million tons in 1960s to 31 million tons in 1980s and moreover 58 million tons in 1995s (Banb and baanata, 1996). The half of the fertilizer used in the developing world is consumed at East Asia. In 1996, FAO proclaimed that the increased in chemical fertilizer use is now a big problem in the world (IFPRI, 1996). Most chemical fertilizers used in modern agriculture mainly contain Nitrogen (N), Phosphorus (P) and Potassium (K) which are called macronutrients. Excess use of macronutrient fertilizers into field soils causes micronutrient imbalance. Nitrate pollution is also a big problem; nitrate formed by excess nitrogenous fertilizers applied in agriculture are leached to the deep soil layer and cause contamination of the groundwater. If the concentration of nitrate in drinking water exceeds 25 mg/l, it may lead to a fatal condition against new - born babies. This symptom is termed "Blue Baby Syndrome". Excess use of fertilizers is not only the problem of plant and animal health but also a big issue on the environmental problem. Eutrophication is typical problem in many developed and developing countries. The application of excess fertilizers into agricultural fields leads to wash off of the nutrient loaded water into nearby lakes causing over-nourishment. This is termed "Eutrophication". Eutrophication in lake ecosystems causes "algal blooms". Algal seriously attest the ecology at lake. Moreover, there are other many kinds of problems

in fertilizer use around the world. Overuse of chemical fertilizer increase the fertilization cost (Bumb and Baanata, 1996), and limit the mineral resources for fertilizer such as phosphate rock. In Japan, the excess accumulation of phosphorus (P) into agricultural soil due to the overuse of P fertilizer is well known (Mishima et al, 2010). Recently, due to the increasing fertilization cost, decrease of P fertilization has been recommended for Japanese farmers.

In the second chapter in this dissertation, the general effects of excess use of fertilizer on crop yield caused by nutrient accumulation in agricultural soil was studied. Since, there are many phosphorus (P) and potassium (K) accumulation in agricultural field, I argue about the effect of long-term P and K fertilization on crop yield in northern Japan in the chapter. On the other hand, in the developing country, farmers have another problems. In Mongolia soil degradation is becoming a very serious agricultural problem in Mongolia. In the third chapter, I focused on the fertilizer use in Mongolian agricultural field. I argue about the effective application method of both an animal manure and a chemical fertilizer for the sustainable agriculture in Mongolia.

As another aspect, P fertilizer is known as potential accumulation source of heavy metals like cadmium, arsenic, and selenium (Se) (Nakamaru et al., 2008). Though no harmful effect of these heavy metals from P fertilizer on crops was reported, we have to know the potential effects of these metals associated with fertilization for sustainable and safe agricultural production. In particular, there is few works on Se effect by fertilizer. In this dissertation, I firstly focused on the Se behavior in P fertilizer. Because Se has both toxic effects and beneficial effects on plant and animals, the Se uptake by crops is important for human health. In the fourth and fifth chapter, I argue about the effect of long-term phosphorus fertilization on Se in soil and also about Se uptake by upland crops in northern Japan.

Chapter II. Effects of three years of continuous no P and no K fertilization under manure application on crop yields and soil chemical properties in northern Japan, Hokkaido

II.I. Introduction

The Abashiri area (44.0° North, 144.2° East), in Hokkaido Prefecture is one of the most important agricultural areas in northern Japan. Most of the agricultural soil in this area has highly accumulated available phosphorus (P) and potassium (K) due to long-term fertilization. Yoshida et al. (2005) reported that no decrease of yield was observed for sugar beet when P and K were not applied in one year of cultivation in the Abashiri area. On Japanese farms, reducing P fertilization application is a recent trend. Mishima et al. (2010) reported that the average P fertilizer use in Japan decreased from 315 kg P_2O_5 ha^{-1} in 1985 to 227 kg P_2O_5 ha^{-1} in 2005, and P efficiency increased from 15.0% in 1985 to 20.1% in 2005. Though the Hokkaido Prefectural government has also recommended reducing P/K fertilization, many farmers have tended to continue conventional P/K fertilization because of the fear of the decline of yield and limited data about the long-term effects of low P/K fertilization. In order to test the possibility for decreased P/K fertilization, I evaluated the effects of continuous low or no P/K fertilization on crop productivity with a field experiment. In this chapter, under three years of continuous decreased P/K fertilization, the crop yield, P/K uptake of crops, soil available P/K amount, and changes of soil P fraction (Al bound P, Fe bound P, Ca bound P) were measured for the fields of the two soil types.

II.II. Materials and Methods

In the Abashiri area, the root distribution of subsoil was identified as one of the most important factors influencing crop productivity (Itoh et al, 2009), and it was considered that the effective root depth affected the P and K availability to crops. Therefore, to test the effects of root distribution, four upland fields in the Abashiri area having two types of soil, Andosol and Cambisol, were used. The soil profile and root distribution of each field were investigated in 2009.

According to the major crop rotation system used in the Abashiri area, sugar beet (*Beta vulgaris* ssp. *vulgaris*), potato (*Solanum tuberosum* L.), winter wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.) were cultivated in this experiment. Four fertilization methods were used: i) Conventional NPK application, ii) half P fertilization (P 1/2), iii) no P fertilization (-P), and iv) no P and no K (-P -K) fertilization. The experiment was started in May 2009, and each fertilization method was continued until November 2011. At the Urashibetsu B field in particular, in 2010, oat (*Avena sativa* L.) was cultivated as green manure and plowed back into the field and so not harvested. The fertilization method and crop rotation system are summarized in Table 2-1. These four treatments were applied as four replicates in a randomized block design, resulting in a total of 16 experimental plots each in Urashibetsu A, B, Yasaka A and B field. Nitrogen (N) was added as Chilean saltpeter for sugar beet, and as ammonium sulfate for other crops. P and K were added as superphosphate and potassium chloride, respectively.

According to the conventional fertilization method of this area, cow manure (average N, P_2O_5, K_2O content = 1.4, 1.5 and 2.6%) was applied as 30 Mg ha^{-1} every three years after the wheat harvest.

After the cultivation, the crop yield and P and K uptake by plant were measured. Soil was sampled during cultivation. Soil samples taken from a depth of 0 to 20 cm were collected from each of the 16 plots in each of the field sites; soil was sampled monthly in the plant growing season (May to October) from 2009 to 2011.

Soil available P was measured by the troug Method using pH 4 $(NH_4)_2SO_4$ – H_2SO_4 solution as an extracted (Troug 1930; Blakemore et al., 1981). The truog method was used because it has been shown to be a suitable method for estimating plant available P of Japanese Andosoil (Kato et al., 1995). The Al-P, Fe-P and Ca-P were measured by the sequential extraction method using 1 mol L^{-1} NH_4F for Al-P mol L^{-1} NaOH for Fe-P,

Table 2-1 Crop rotation system and fertilization (kg ha^{-1}) method of each test field in the experiment from 2009-2011

	Manure [1] (Sep.2008)			2009			2010						2011		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O	N	P_2O_5	K_2O				N	P_2O_5	K_2O
Urashibetsu	Applied in 2008			Sugar beet			Potato						Winter wheat		
Conventiona	420	450	780	160	250	160	100	180	130				100	150	100
P 1/2	420	450	780	160	125	160	100	90	130				100	75	100
-P	420	450	780	160	0	160	100	0	130				100	0	100
-P -K	420	450	780	160	0	0	100	0	0	Green manure[2]			100	0	0
Urashibetsu B				Potato			Oat as green manure			N	P_2O_5	K_2O	Winter wheat		
Conventional				100	180	130	60	0	0	22	9	48	100	150	100
P 1/2				100	90	130	60	0	0	22	9	48	100	75	100
-P				100	0	130	60	0	0	22	9	48	100	0	100
-P -K				100	0	0	60	0	0	22	9	48	100	0	0
Yasaka A	Applied in 2008			Sugar beet			Potato						Barley		
Conventiona	420	450	780	160	250	160	100	180	130				60	100	80
P 1/2	420	450	780	160	125	160	100	90	130				60	50	80
-P	420	450	780	160	0	160	100	0	130				60	0	80
-P -K	420	450	780	160	0	0	100	0	0	Manure (Sep.2010)			60	0	0
Yasaka B				Potato			Winter wheat			N	P_2O_5	K_2O	Sugar beet		
Conventional				100	180	130	100	150	100	420	450	780	160	250	160
P 1/2				100	90	130	100	75	100	420	450	780	160	125	160
-P				100	0	130	100	0	100	420	450	780	160	0	160
-P -K				100	0	0	100	0	0	420	450	780	160	0	0

[1]Manure (average N, P_2O_5, K_2O content =1.4, 1.5 and 2.6%) 30 Mg ha^{-1} was applied to Urashibetsu A and Yasaka A before the experiment. For Urashibetsu B and Yasaka B field, same amount of manure was applied in 2007 and 2010, respectively.

[2]Green manure (N, P_2O_5, K_2O content =1.4, 0.6 and 3.1%[4]) was applied at average yield of Urashivetsu B in 2010 (1.6 Mg ha^{-1}).
In the table negative results were due to the manure application interval in September 2008 to 2010. (Urashibetsu-B and Yasaka-B had no manure application in 2008).

Table 2-2 Soil properties for four test fields at the beginning of the experiment (2009) and root number density

	pH (H_2O)	Available P_2O_5[1] (mg P_2O_5 kg^{-1})	Phosphate adsorption coefficient[1)]	Exchangeable K_2O[1] (mg K_2O kg^{-1})	Root number density[2] (roots cm^{-2})
Urashibetsu A (Light-colored Andosol)					**Sugar beet**
0-20 cm	**6.5**	**193**	**1351**	**1175**	**0.29**
20-40 cm	**6.2**	**202**	**1329**	**1398**	**0.60**
40-60 cm	**6.2**	**100**	**1338**	**1243**	**0.45**
60-80 cm	**6.3**	**13**	**752**	**615**	**0.13**
Urashibetsu B (Light-colored Andosol)					**Potato**
0-20 cm	**5.5**	**297**	**1233**	**838**	**0.36**
20-40 cm	**5.9**	**337**	**1164**	**907**	**0.36**
40-60 cm	**6.4**	**29**	**784**	**908**	**0.34**
60-80 cm	**6.3**	**32**	**669**	**723**	**0.08**
Yasaka A (Gray Upland soil (Cambisol))					**Sugar beet**
0-20 cm	**6.9**	**538**	**1233**	**465**	**0.52**
20-40 cm	**6.7**	**485**	**1164**	**449**	**0.36**
40-60 cm	**6.5**	**5**	**784**	**145**	**0.18**
60-80 cm	**6.5**	**7**	**669**	**180**	**0.06**
Yasaka B (Gray Upland soil (Cambisol))					**Potato**
0-20 cm	**5.6**	**458**	**1092**	**679**	**1.18**
20-40 cm	**5.8**	**368**	**1111**	**691**	**0.47**
40-60 cm	**6.5**	**15**	**761**	**665**	**0.26**
60-80 cm	**6.6**	**8**	**531**	**308**	**0.07**

[1]Results are for the -P-K fertilization method of each field in June 2009.

[2] Results are for the Conventional fertilization method of each field in August 2009.

II.III. Results and Discussion

II.III.I. Soil properties of experiment fields

The soil chemical properties and root distribution patterns (root number density) of the four test fields are shown in Table 2-2. According to the soil profile survey of each field in 2009, it was confirmed that the Andosol fields (Urashibetsu A, B) had a deep root zone (up to 1m depth), while in the Cambisol fields (Yasaka A, B), the root zone was limited by a clayey B horizon at 40 cm depth. Yasaka A and B were Cambisol fields and their root density was low in the subsoil. Soils in tested fields were found to be acidic and both exhibited high phosphate adsorption coefficients (1164-1351 mg P_2O_5 adsorbed to 100g of soil) in the 0-40cm depth.

II.III.II. Effects of decreased P/K fertilization on crop yield

The crop yields of each field in the experiment from 2009-2011 are shown in Table 2-3. For the three years, except for Urashibetsu B field in 2009, there was no significant statistical difference among the yields with four fertilizations for all the fields (The results are presented as the average of four replicates. The statistical software program used for ANOVA test by Bonferroi's method was "Uchu-Yuki's UFO test version 1.0"). In the Cambisol field (Yasaka A), average potato yield was lower at the end of the second year for -P and P 1/2 methods. In the third year, no decrease of yield for the -P -K method was observed in the Andosol fields(Urashibetsu A and B), while in the Cambisol fields (Yasaka A and B), the barley and sugar beet yields of the –P –K method were relatively lower than those of the –P method. This result could be due to the lower exchangeable K amount in Yasaka A and B fields than in Urashibetsu A and B fields (Table 2-2). However, even though Yasaka A and B fields had more available P (400-700 mg P_2O_5 kg^{-1}) than Urashibetsu A and B fields (200-500 mg P_2O_5 kg^{-1}), the decrease of crop yield with decreased P/K fertilization was more likely to occur in the Yasaka A and B fields. For the P uptake by plants, root length is the dominant factor controlling P uptake because of the low P solubility in soil solution (Barber, 1984). Possibly the limited root distribution in Yasaka A and B fields could be the major factor to explain the lower yield, due to the lower efficiency of P uptake. These results showed the possibility of decreased P/K fertilization in Abashiri area. For the recommendation to famers, however the risk of the decreased fertilization should be considered carefully. We thought that the soil property of Cambisol field could be one of the risk factors.

II.IV.III. Effects of decreased P/K fertilization on soil available P and exchangeable K content

The changes of soil available P and exchangeable K during the experiment are shown in Table 2-4. For soil available P, though the Conventional fertilization method tended to result in higher values, for Urashibetsu A and Yasaka A fields, the values increased in 2010, and then decreased in 2011, for all four fertilization methods. For Urashibetsu B and Yasaka B fields, the values increased in 2011. These trends could be attributed to the application of animal manure and green manure. In 2008, animal manure was added to the soil of Urashibetsu A and Yasaka A fields, and in 2010, green manure and animal manure was applied for Urashibetsu B and Yasaka B, respectively (Table 2-1). The increase of available P would be explained by the mineralization of organic P in the manure. For the soil exchangeable K content, though irregular changes were observed for all fields from 2009 to 2011, the –P –K fertilization method gave relatively lower values than the other methods. During the cultivation from 2009 to 2011, both values of available P and exchangeable K were within or beyond the recommended values set by the Hokkaido Prefectural government (100-300 mg P_2O_5 kg^{-1} and 150-300 mg K_2O kg^{-1}, respectively). In the Abashiri area, another field cultivation experiment of potato without P/K fertilization from 2007 to 2009 also showed that no P fertilization could not decrease soil available P immediately (Kikuchi et al., 2012). In that experiment, the annual decreases of available P and exchangeable K were -6 mg P_2O_5 kg^{-1} and 88 mg K_2O kg^{-1}, respectively.

II.IV.IV. Changes of phosphorus fraction of soil during 2009-2011

Changes of soil Al-P, Fe-P, Ca-P are shown in Table 2-5. While soil total inorganic P and Al-P amounts did not change clearly for any of the fields, Ca bound P was increased during three years, and the increase was especially obvious for Urashibetsu A and Yasaka A fields. The amount of Ca-P fraction increased in Urashibetsu A and Yasaka A fields was around 300 mg P_2O_5 kg^{-1}, and was almost the same level as the increase of soil available P. These increases of Ca-P and available P could be explained by the manure application in the Urashibetsu A and Yasaka A fields. On the other hand, the amount of Fe-P decreased, and the decrease was 253 mg P_2O_5 $kg^{-1}$and 236 mg P_2O_5 kg^{-1} for Urashibetsu A, and Yasaka A fields, 93 mg P_2O_5 kg^{-1} and 142 mg P_2O_5 kg^{-1} for Urashibetsu B, and Yasaka B fields (average of four plots), respectively. This would be explained by the manure application in 2008 for Urashibetsu A, and Yasaka A fields.

Many studies have reported a similar effect of organic fertilizer on soil P fraction. Hirata et al. reported that application of manure decreased Fe-P fraction in a 9-year continuous experiment on a Japanese upland Andosol field (Hirata et al; 1999). Li et al. also reported that the amount of Fe-P decreased with the application of organic fertilizer in a pot experiment; they explained that the manure application increased organic P mineralization due to microbial activity (Li et al., 2012), which was also reported by Takeda et al., (2009) and Li et al, (2012), also mentioned that the reduced P adsorption contributed to increased P availability (Li et al., 2012). The present field experiment results also suggested that organic fertilizer could enhance soil P availability not only as a P source but also as a contributor to increase P availability.

II.IV.V. The P and K uptake of crops and the P and K balance of the tested fields

The P and K uptake of crops and the balance of P and K in the experiment are shown in Table 2-6. The P and K balance was calculated by the P and K uptake and the fertilized P and K amount shown in Table 2-6. The uptake values were calculated for sugar beet root, potato tuber, wheat grain and shoot, and barley grain and shoot. The P balance data did not accounted the green manure application in Urashibetsu B field because there was no input and no output of P and K by green manure. For P, the P uptake values did not decrease clearly with the decreased P fertilization except for the potato P uptake for Yasaka A field in 2010. However, the P balance was a negative value for the Urashibetsu B and Yasaka B fields in 2010. The value of Yasaka B field turned to be positive in 2011 but the value of Urashibetsu B field remained negative in 2011. These results were due to the manure application in 2008 and 2010 (Table 2-1) and corresponded to the results of the changes in soil available P. For the K uptake by crops of Urashibetsu A and Yasaka B field in 2011, the values for the –P–K fertilization method tended to be lower than the other fertilization methods. K balance also reflected the manure application; the Urashibetsu B and Yasaka B fields had negative values from 2010. These P/K balance and soil available P and exchangeable K data showed that the conventional manure application (10 Mg ha^{-1} y^{-1}) could maintain soil P and K amount without fertilization in Abashiri area. With the results of crop yield data in Urashibetu area, winter wheat yield of no P and/or no K plots in Urashibetsu A and Urashibetsu B field were the same level though the P and K balance was negative in Urashibetsu B field. This suggested that the soil accumulated P was sufficient to maintain wheat productivity even under the three years of no P and/or no K application.

Table 2-3 The crop yield (Mg ha^{-1}) [1] of each test field in the experiment from 2009-2011

Fertilization method	2009		2010	2011	
Urashibetsu A	Sugar beet (root)	(Sugar production) [2]	Potato (tuber)	Winter wheat (grain)	
Conventional	71.1±2.3a[3]	(11.5±0.8a)	23.1±4.1a	9.4±1.9a	
P 1/2	69.0±8.2a	(11.1±1.6a)	23.1±1.2a	9.0±2.7a	
-P	74.8±4.3a	(12.1±0.7a)	23.6±3.9a	8.3±1.9a	
-P -K	77.0±10.7a	(12.0±1.5a)	28.2±3.5a	9.4±1.6a	
Urashibetsu B	Potato (tuber)		Oat as green manure	Winter wheat (grain)	
Conventional	63.0±9.8ab		1.44±0.31a	9.8±3.1a	
P 1/2	75.2±14.7a		1.87±0.55a	10.6±2.9a	
-P	67.2±5.1a		1.72±0.49a	8.2±2.9a	
-P -K	54.3±11.6b		1.20±0.25a	11.0±1.6a	
Yasaka A	Sugar beet (root)	(Sugar production) [2]	Potato (tuber)	Barley (grain)	
Conventional	68.0±3.4a	(11.3±0.7a)	58.7±14.6a	6.1±2.4a	
P 1/2	68.3±9.7a	(11.5±1.7a)	55.6±4.8a	5.6±2.8a	
-P	66.1±9.8a	(11.2±1.4a)	50.4±6.2a	6.3±1.8a	
-P -K	61.3±3.6a	(10.4±0.7a)	49.0±5.0a	5.5±1.0a	
Yasaka B	Potato (tuber)		Winter wheat (grain)	Sugar beet (root)	(Sugar production) [2]
Conventional	43.1±12.4a		5.7±0.7a	64.9±11.9a	(9.8±2.1a)
P 1/2	45.0±11.3a		5.6±0.6a	67.2±15.6a	(10.1±1.8a)
-P	44.4±10.9a		5.6±0.9a	62.7±26.6a	(9.3±3.6a)
-P -K	52.0±4.0a		5.5±0.7a	59.1±12.6a	(8.8±2.0a)

[1]Results are the average value and ± standard deviation of four replications. [2] For sugar beet, sugar production is also indicated.
[3]Values followed by different letters were found to be significantly different when comparing four fertilizations (ANOVA; $P<0.05$ by Bonferroni 's method).

Table 2-4 Soil available P[1] and exchangeable K[1] (0-20 cm soil) of each plot at the beginning and the end of the cultivation in 2009-2011

	Available P (mg P_2O_5 kg^{-1})						Exchabgeable K (mg K_2O kg^{-1})					
	2009		2010		2011		2009		2010		2011	
Urashibetsu A	29-May	15-Oct	25-May	11-Aug	16-May	21-Jul	29-May	15-Oct	25-May	11-Aug	16-May	21-Jul
Conventional	237	180	426	345	296	228	1350	973	1010	1270	880	1160
P 1/2	238	168	366	470	277	284	1216	1228	1190	1090	1120	1431
-P	245	193	228	359	209	263	1322	1053	1060	1040	1340	1341
-P -K	193	173	224	297	191	196	1175	1228	890	940	1130	1325
Urashibetsu B	29-May	15-Oct	21-May	11-Sep	16-May	21-Jul	29-May	15-Oct			16-May	21-Jul
Conventional	596	325	109	147	237	273	1300	811			910	759
P 1/2	375	233	95	130	238	237	1247	784			970	784
-P	303	200	138	133	237	215	1250	910			1020	811
-P -K	297	203	164	135	244	250	838	701			940	974
Yasaka A	2-Jun	16-Oct	25-May	30-Sep	2-Jun	28-Jul	29-May	15-Oct	25-May	11-Aug	2-Jun	28-Jul
Conventional	708	529	754	789	478	471	705	462	910	380	572	346
P 1/2	583	496	674	671	525	421	693	500	600	260	377	391
-P	479	373	589	556	444	385	833	457	740	380	387	343
-P -K	538	406	604	705	449	408	465	333	570	170	295	246
Yasaka B	2-Jun	16-Oct	22-May	20-Jul	9-Jun	13-Oct	29-May	15-Oct	22-May	20-Jul	9-Jun	13-Oct
Conventional	623	400	476	678	476	619	594	612	610	566	680	677
P 1/2	521	380	461	468	555	754	627	556	590	573	770	689
-P	447	371	444	455	511	453	610	596	630	571	630	611
-P -K	458	344	407	456	420	405	679	520	620	575	570	435

[1]Results are the average value of four replications.

Table 2-5 Soil phosphorus fractionation[1] (0-20 cm soil) of each plot at the beginning and the end of the cultivation in 2009-2011

	Al- P (mg P_2O_5 kg^{-1})						Fe- P (mg P_2O_5 kg^{-1})						Ca- P (mg P_2O_5 kg^{-1})					
	2009		2010		2011		2009		2010		2011		2009		2010		2011	
Urashibetsu A	29-May	15-Oct	25-May	11-Aug	16-May	21-Jul	29-May	15-Oct	25-May	11-Aug	16-May	21-Jul	29-May	15-Oct	25-May	11-Aug	16-May	21-Jul
Conventional	1480	1571	1807	1914	1784	1563	732	713	435	513	589	512	223	238	489	529	421	491
P1/2	1503	1443	1872	2335	2211	1406	689	683	467	533	481	402	234	227	526	682	511	554
-P	1629	1485	1495	1992	1935	1780	762	730	482	476	522	490	252	207	392	523	540	536
-P-K	1349	1312	1389	1731	1584	1511	650	640	435	497	504	512	200	196	327	420	500	328
Urashibetsu B	29-May	15-Oct	21-May	11-Sep	16-May	21-Jul	29-May	15-Oct	21-May	11-Sep	16-May	21-Jul	29-May	15-Oct	21-May	11-Sep	16-May	21-Jul
Conventional	2121	1900	1990	2010	1829	1829	674	732	601	526	365	375	403	318	255	263	435	414
P1/2	1967	1832	1990	2240	1822	1813	709	750	607	528	373	483	260	278	249	257	411	385
-P	1768	1737	2060	2180	1808	1441	687	734	578	533	370	483	241	238	267	265	362	365
-P-K	1700	1636	1730	2270	1703	1311	640	668	551	532	379	362	246	261	265	263	383	348
Yasaka A	2-Jun	16-Oct	25-May	30-Sep	2-Jun	28-Jul	2-Jun	16-Oct	25-May	30-Sep	2-Jun	28-Jul	2-Jun	16-Oct	25-May	30-Sep	2-Jun	28-Jul
Conventional	1696	1551	1553	1735	1290	1520	658	633	431	405	388	471	315	285	517	561	447	490
P1/2	1380	1437	1327	1477	1140	1340	630	676	405	308	366	421	263	250	447	508	425	419
-P	1032	1296	1384	1383	1080	1380	613	630	355	303	305	385	269	192	494	528	414	407
-P-K	1013	1371	1384	1627	1180	1290	599	624	364	338	378	408	311	231	466	589	416	409
Yasaka B	2-Jun	16-Oct	22-May	20-Jul	9-Jun	13-Oct	2-Jun	16-Oct	22-May	20-Jul	9-Jun	13-Oct	2-Jun	16-Oct	22-May	20-Jul	9-Jun	13-Oct
Conventional	1229	1241	1241	1255	1402	1298	658	689	477	506	478	719	235	279	395	404	450	399
P1/2	1294	1112	1211	1180	1340	1451	630	650	486	484	463	510	289	256	389	357	400	432
-P	1145	1080	1189	1090	1185	1041	613	600	477	438	431	457	270	277	366	338	400	331
-P-K	1148	1073	1094	1054	1157	972	599	636	492	453	566	473	283	261	354	345	359	302

[1]Values are the average of four replications.

Table 2-6 The phosphorus and potassium uptakes and balances [1] by crops (kg ha^{-1}) of each test field

	P_2O_5 uptake			P_2O_5 balance			K_2O uptake			K_2O balance		
Field and plot	2009	2010	2011	2009	2010	2011	2009	2010	2011	2009	2010	2011
Urashibetsu A	Sugar beet	Potato	Winter wheat				Sugar beet	Potato	Winter wheat			
Conventional	62	65	212	638	753	691	134	277	265	806	658	494
P 1/2	55	64	169	520	546	452	154	286	323	786	631	408
-P	60	66	220	390	324	104	181	279	445	759	611	266
-P -K	57	67	164	393	326	162	154	283	224	626	343	119
Urashibetsu B	Potato	Green manure	Winter wheat				Potato	Green manure	Winter wheat			
Conventional	105		158	75	75	67	329		256	-199	-199	-355
P 1/2	121		192	-31	-31	-148	382		256	-252	-252	-407
-P	108		164	-108	-108	-272	361		185	-231	-231	-316
-P -K	93		137	-93	-93	-230	309		210	-309	-309	-520
Yasaka A	Sugar beet	Potato	Barley				Sugar beet	Potato	Barley			
Conventional	63	104	321	637	713	492	107	288	178	833	675	577
P 1/2	70	90	298	505	505	257	119	279	157	821	672	596
-P	64	76	367	386	310	-57	111	250	173	829	709	616
-P -K	56	70	385	394	324	-61	79	256	173	701	445	272
Yasaka B	Potato	Winter wheat	Sugar beet				Potato	Winter wheat	Sugar beet			
Conventional	62	231	117	118	37	620	156	239	141	-26	-165	634
P 1/2	80	214	120	10	-129	326	211	247	123	-81	-228	589
-P	81	190	114	-81	-271	65	212	231	136	-82	-213	591
-P -K	98	237	106	-98	-335	9	274	281	110	-274	-555	115

[1]Phosphorus and potassium balances were calculated as the difference between the accumulation of nutrient amount fertilized (see Table 2-1) and the uptake for each year.

II.V. Conclusion

The crop yield in four fields did not change significantly when decreased P/K fertilization was used during a 3-year experiment regardless of the different soil type. For the soil available P/K, the accumulated P/K in soil did not decrease significantly for the three years of no P and no K fertilization, and was increased by the manure application. Therefore the decreased P and no K fertilization method should be started the next year after manure application.

II. VI. Summary

The Abashiri area in Hokkaido Prefecture is one of the most important agricultural areas in northern Japan. Due to long-term fertilization, most of the agricultural soil in this area has highly accumulated available P and K. In addition to this, typically about 450 kg P_2O_5 ha^{-1} and 780 kg K_2O ha^{-1} have been applied with 30 Mg ha^{-1} of animal manure every three years. In order to assess the possibility of decreased P and K fertilization using this accumulated P and K, we evaluated the effects of three years of continuous low or no P and K fertilization on crop productivity by a field experiment. From 2009 to 2011, sugar beet, potato, wheat and barley were cultivated using the major crop rotation system in this area. Four fertilization methods were used: i) Conventional NPK application, ii) half P fertilization, iii) no P fertilization, and iv) no P and no K fertilization. Two Andosol fields (Urashibetsu A, B) and two Cambisol fields (Yasaka A, B) were used for this study. 30 Mg ha^{-1} of manure was applied to Urashibetsu A and Yasaka A field before the experiment. For Urashibetsu B and Yasaka B field, the same amount of manure was applied in 2007 and 2010, respectively. In Urashibetsu B field in particular, in 2010, oat was cultivated as green manure and plowed back into the field. The crop yield, soil available P and exchangeable K amounts, soil P fractions (Al bound P, Fe bound P, Ca bound P) were measured. As a result, almost no significant effects of P/K fertilization on crop yield were observed during three years. Due to manure application, soil available P and exchangeable K amount did not decrease during of the three years of no P and no K application. Manure application for Urashibetsu A and Yasaka A fields also increased Ca bound P fraction and decreased Fe bound P fraction. These results suggested that manure application increased soil P availability not only as an organic P source but also as a contributor to Fe bound P utilization. From these results, we considered that decreased or no P/K fertilization method should be started the next year after manure application in Abashiri area.

Chapter III. General effect of chemical fertilizer and animal manure use in Mongolian Kastanozem farm

III.I. Introduction

Mongolia is situated in central Asia and shares borders with Russia and China. It covers an area of 1.5 million square kilometers and has a population of 2.8 million people. Its arable soils are typically light and silty, are present to a depth of around 30 cm, have high organic matter content of 3 to 4%, and are moderately acidic to neutral with pH value of 6.0 to 7.0 (Batjargal, 1992). Usually these soils are rich in calcium, but deficient in phosphate (Batjargal, 1992). The relatively light nature of the soils results in low moisture retention and this characteristic makes them more prone to erosion. The impact to human activities in Mongolia has led to increasing soil erosion not only on cultivated land but also pasture land, which has led to serious environmental problems. Recently, in Mongolia, soil degradation has appeared as a major limitation to increasing the country's food production. It was reported that impact of grazing on vegetation in southern Mongolian was apparent though it was still smaller than the effect of high inter-annual variability in precipitation (Stumpp et al., 2005; Wesche et al., 2010). Therefore, improvement of farming methods for land production is needed. Also, in the China Autonomous Region of Inner Mongolia, Land degradation of grassland is advancing over wide areas due to overgrazing (Akiyama et al., 2007). To find technological solutions for land degradation, some trials have been made in Inner Mongolia, such as conversion of pasture from grazing to hay-making pasture (Kawanaba et al., 1991), use of crop rotation and crop residue management (Wang, 2002), use of animal manure (Idota et al., 2000), and nitrogen fertilizer application (Wang et al., 2002; Wang et al., 2005). In the case of China, according to Brogaard and Xueyong (2002), the Chinese Communist Party initiated economic reforms in 1978, and farmers applied chemical fertilizers excessively in the following 30 years for short-term economic sustainability rather than long-term environmental sustainability. However, in Mongolia, many farmers have never used any mineral fertilizers or any pesticides due to insufficient supplies or lack of financial sources; besides most have used no organic manure for improvement of the soil fertility and increase of the yield. Therefore, we thought that the use of chemical fertilizers was not suitable for maintaining land productivity in Mongolia. From 2010 to 2012, we carried out a study to utilize a crop rotation system and animal manure to make Mongolian agriculture more sustainable. In this study, I used manure made from sheeps and goats dung because these animals are most common livestock in Mongolia. In the winter, dung of seeps and goats were accumulated and naturally fermented for three month, and were used for the present study.

III.II. Materials and Methods

The field study was conducted in the Nart Experimental Farm of the Mongolian State University of Agriculture (48°36' 42.3" North, 106°29' 20, 7"East). The soil of this field was classified according to the FAO-UNESCO classification system as a Kastanozem soil. During 2010 to 2012, as an appropriate alternative to a conventional agricultural system (FAO-UNESCO.,1990) which is spring wheat single cropping, I tested Mongolian crop rotation system by using potato (*Solanum tuberosum* L.), rye (*Secale cereale* L.), turnip (*Brassica rapa* L. var. glabra) and pea (*Pisum sativum* L.). In the field experiment, three fertilization methods were used: i) no fertilization (control 1 and control 2 plots, for control 1, goat pasturage area was used for cultivation and goat dung was distributed for one year); ii) application of manure of 40 Mg $ha^{-1}y^{-1}$ (688 kg N $ha^{-1}y^{-1}$, 184 kg P_2O $ha^{-1}y^{-1}$ and 180 kg K_2O $ha^{-1}y^{-1}$) (manure plot); and iii) application of chemical fertilizer of 90 kg N $ha^{-1}y^{-1}$, 90 kg P_2O_5 $ha^{-1}y^{-1}$ and 90 kg K_2O $ha^{-1}y^{-1}$ (NPK plot). In the manure plot, I used manure made from sheeps and goats dung in Nart area around the Nart experimental farm. Major and minor nutrients amount of the manure used for the study was shown in Table 3-1. Nitrogen content of manure was analyzed by NC analyzer (Smigraph NC-220F) and P was analyzed by colorimetry using ammonium molybdate as a reagent. The other nutrients amounts of manure was measured by Atomic Absorption Spectrometry (Thermo Fisher, iCE 3000) following digestion of the sample with $HClO_4$-HNO_3-HF. For the most of nutrients, manure used in Nart farm (Mongolia) showed favorable concentration level, except of zinc. The low zinc amount of the manure used in Nart farm should be due to the feed and type of animals (sheep and goat). However, no symptoms of the deficiency of Fe, Mn, Zn, Cu, and Co was observed for potato, rye, turnip and pea in Nart farm. Thus, we focused on the effect of soil major nutrients in this study. Due to the small precipitation rate, decomposition rate of organic fertilizer was expected to be low in Mongolia. To observe clearly the increase in the amount of available nutrients by manure application in the three years of studying period, high amount of nutrients (668 kg N K_2O $ha^{-1}y^{-1}$) have been applied by the manure. This manure application rate (40 Mg ha^{-1} y^{-1}) is about three times higher than that in Hokkaido, Japan. Figure 3-1 shows the plot design and crop rotation of the field study. The experimental field had been separated into three areas, and three crop rotation sequences had been made for each area. Crops of the first, second and third

year were turnip-potato-rye for area-1, potato-rye-pea for area-2 and rye-pea-turnip for area-3. In the field study, crop yield and soil pH(H_2O), CEC, available N, available P, and exchangeable K, Ca, and Mg were measured after the harvest of each year. Yield of the crops were calculated from the fresh weight of edible parts of sampled plants from the four selected area (3.3 m^2) in the tested field. Soil samples were collected from each of the 16 plots every September from 2010 to 2012 at a depth of 0-20 cm, 20-40 cm, 40-60 cm and 60-80 cm. Crop yield was also measured each September. Soil available N amount was measured by 1 mol L^{-1} KCl extraction after a 4-week incubation. The available soil P was extracted by the Truog method using a pH 4 $(NH_4)_2SO_4$-H_2SO_4 solution (Troug., 1930, Blakemore., 1981) and by the Olsen method using 0.5 mol L^{-1} $NaHCO_3$ (pH 8.5) as extractant (Olsen, 1982). The CEC and exchangeable K, Ca, and Mg amounts were determined by the Schollenberger method (Schollenberger, 1945). Soil moisture was measured soil volumetric water content by the soil volumetric every month in plant growth season (from May to September).

Figure 3-1. Plot design of the experimental field in Nart farm from 2010 to 2013

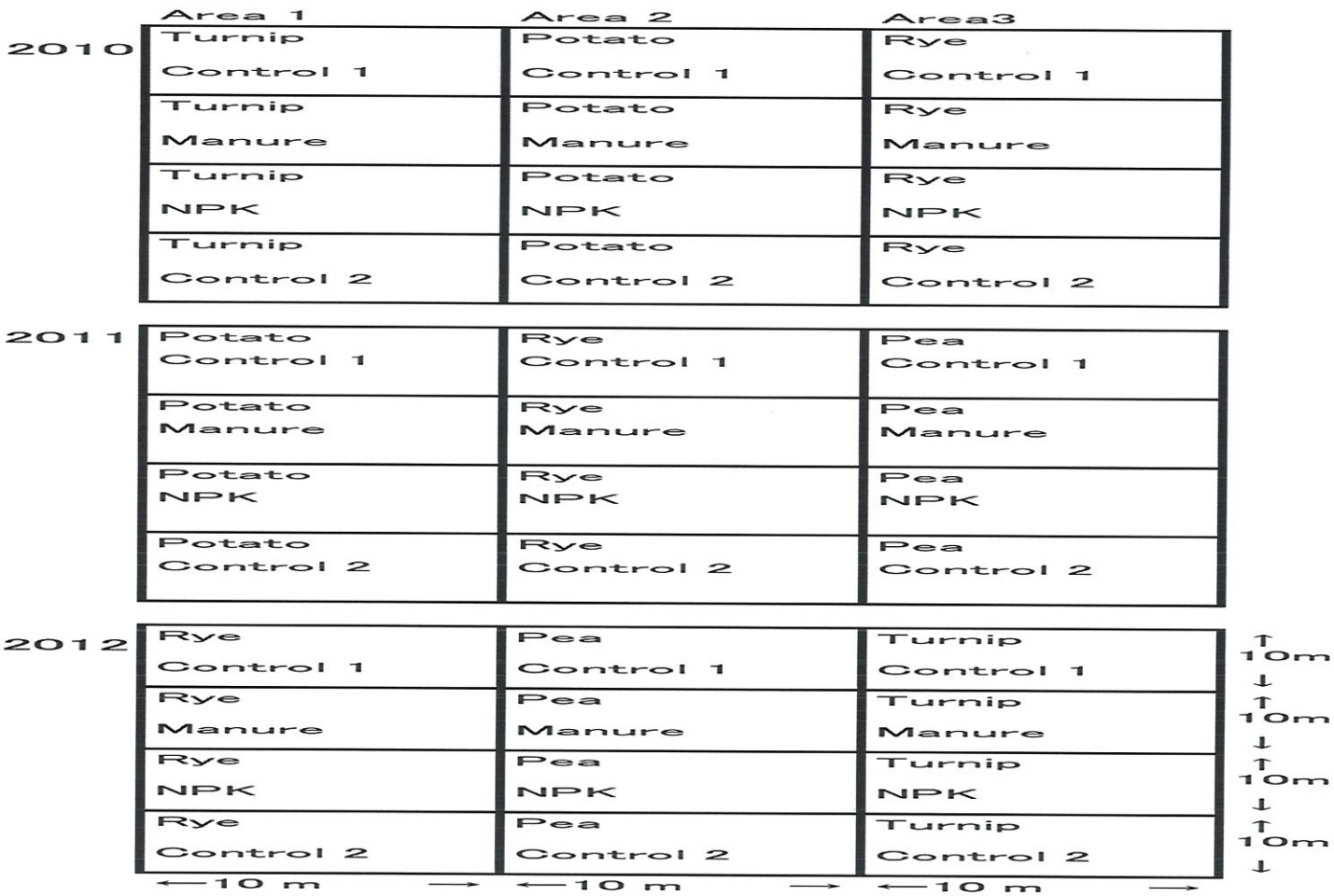


Table 3-1. Major and minor nutrients amount of manure used in Nart farm

Major nutrients (%)		N	P	K	Ca	Mg
Nart farm	Mean[a]	1.67	0.46	0.45	1.93	0.54
	SD[a]	0.21	0.09	0.23	0.20	0.07
		Applied nutrient (kg ha^{-1}) with manure (40 Mg ha^{-1} y^{-1}) in Nart farm				
		668	184	180	772	216
Minor nutrients (mg kg^{-1})		Zn	Cu	Mn	Cr	Ni
Nart farm	Mean[a]	78	21	439	146	41
	SD[a]	3	2	42	64	10
		Applied nutrient (kg ha^{-1}) with manure (40 Mg ha^{-1} y^{-1}) in Nart farm				
		3.10	0.85	17.55	5.85	1.63

[a] Values are mean of two replicated values and the standard deviations.

III.III. Results and Discussion

III.III.I. Soil properties

Kastanozem soil has relatively high productivity and includes a large amount of Ca carbonate (FAO-UNESCO, 1990). Soil properties measured for the experimental field are shown in Table 3-2. Soil pH at the Nart farm was 7.9-8.1 for surface soil (0-20cm) and 8.7-8.9 for the subsoil (20-80cm). For surface soil, during the three years, CEC value, soil total C, available N, Truog-P, Olsen-P, and exchangeable K contents in the experimental field were 88-785 (average; 100) $mScm^{-1}$, 1.1-1.9 (average; 1.6) C%, 177-219 (average; 177) mg N kg^{-1}, 47-119 (average; 59) mg P kg^{-1}, 4.3-18.7 (average; 8,6) mg P kg^{-1}, and 83-210 (average:80) mg K kg^{-1}, respectively. For soil available P values, Truog-P values were higher than Olsen-P values. This indicated that the acid-soluble soil P fraction was dominant in the Nart farm soil as compared to the alkaline-soluble soil P. The chemical form of Truog-P may be a Ca-bound P form because the exchangeable Ca amount was very high in this soil. The changes of major nutrient amounts in the three years are shown in Table 3-3. Among measured soil nutrients, the effect of fertilization was observed only for the available N value. Available N, P and exchangeable K content values increased during 2010 to 2012. In 2011 and 2012, the available N value tended to be higher for the manure plot than the other plots, though the differences were not statistically significant. The soil moisture content during the three years is shown in Figure 3-2; due to little precipitation in 2010. The soil moisture in the growing stage (June to September) was lower than the other years, thus the lower decomposition rate of soil organic matter might have caused the low available soil nutrients in 2010. As reported by Wesche et al.,(2010), the effect of high inter annual variability in the precipitation of Mongolia is the dominant factor affecting plant growth. Additionally, the high soil available N content in the manure plot might be caused by the decomposition of the applied manure. However, contribution of chemical fertilizer on soil available N content did not observed clearly. Though the factor of low efficiency of chemical fertilizer is unknown, I think that the competition of nutrient between crops and weeds could be possible reason because the leaching of nutrients was considered to be not so strong under little precipitation in the studied area.

III.III.II. Crop yields from 2010 to 2012

The yield of each crops2010 to 2012 are shown in Table 3-4. They were over wide ranges: 5.1-25.8 Mg ha^{-1} for potato tuber, 1.3-2.2 Mg ha^{-1} for rye grain, and 0.4-18.6 Mg ha^{-1} for turnip root. The yield of potato in this crop rotation system did not exceed the yield in a conventional cropping at Nart farm (25.9±2.7 Mg ha^{-1}) in 2012. Thus, it was considered that the three-year experimental period was not long enough to detect the effect of the crop rotation system on soil productivity. In this crop rotation system, yields of potato and turnip varied greatly between the years while the rye yield was relatively stable. This related to annual variability in precipitation as described above, and the possible effect of weeds. Such annual variation of crop yield would be a large problem in making a crop rotation system with a high diversity of crop species. Though no significant effects on yield were observed for both chemical and organic fertilizer application, the highest yield of potato (in 2010), pea (in 2011), and turnip (in 2012) were observed for manure plots among all treatments. Among soil nutrients, only soil available N content had relationship with crop yield. Available P and exchangeable K amount had no effect on crop yields. Figure 3-3 shows the relationship between soil available N amount and relative crop yield. In these figures, crop yields were normalized using the value of the control 2 plot as 100. Crop yield was positively related to soil available N value in 2010 and 2012. In 2011, no relationship was observed between crop yield and soil available N value due to an unidentified factor or factors. From the observed relationship between soil available N values and crop yields, and the high available N amount in the manure plot, I considered that i) at the Nart farm, soil degradation due to single cropping was not significant in the three years of the field study and ii) to increase the crop yield, amount of soil available N should be increased, farther, iii) animal manure might increase the amount of soil available N and that was more favorable to maintain soil productivity than chemical fertilizer applications.

Table 3-2. Soil properties [a] of each plot in Nart farm (2012)

Plots	Soil depth (cm) and horizons	pH (H_2O)	CEC (μScm^{-1})	T-C (C%)	T-N (mg N kg^{-1})	Available N (mg N kg^{-1})	Available P (mg P kg^{-1})		Exchangeable cations			
							Truog-method	Olsen-method	K	Ca	Mg	Na
									(mg K, Ca, Mg, Na kg^{-1})			
Control 1	0-20 (Ap)	8.04	97	1.56	1522	168	111	13.1	171	920	219	23
	20-40 (B1)	8.66	112	1.37	898	-	65	4.4	94	1768	201	20
	40-60 (B2)	8.72	117	1.28	769	-	56	6	86	3452	231	20
	60-80 (B3)	8.77	126	1.2	577	-	58	5.1	65	3131	238	32
Control 2	0-20 (Ap)	8.14	97	1.59	1561	208	114	17.3	184	1118	206	74
	20-40 (B1)	8.74	114	1.36	769	-	55	4.3	74	1918	205	10
	40-60 (B2)	8.79	785	1.19	534	-	47	5.2	83	4690	208	20
	60-80 (B3)	8.65	123	0.99	408	-	58	5.9	69	1618	280	46
Manure	0-20 (Ap)	7.93	105	1.69	1574	219	115	16.6	210	1236	230	29
	20-40 (B1)	8.69	101	1.02	608	-	61	14.1	69	3216	172	9
	40-60 (B2)	8.69	100	1.28	616	-	50	5.9	117	4348	221	41
	60-80 (B3)	8.71	110	1.19	475	-	53	4.7	78	4102	252	30
NPK	0-20 (Ap)	8.05	105	1.97	1811	177	119	18.7	189	1321	230	12
	20-40 (B1)	8.67	125	1.13	539	-	52	6.2	62	4039	204	46
	40-60 (B2)	8.8	88	1.4	608	-	59	5.3	79	4154	313	191
	60-80 (B3)	8.92	88	1.11	438	-	70	5.1	88	3626	316	14

[a] Data were the arithmetic mean of three areas.

Table 3-3. Changes in soil available nutrients from 2010 to 2012

	Available N [a] (mg N kg^{-1})			Available P [a] (mg P kg^{-1})			Exchangeable K [a] (mg K kg^{-1})		
	2010	2011	2012	2010	2011	2012	2010	2011	2012
Control 1	53±1	82±9	168±17	41±14	76±30	111±23	108±36	93±36	171±20
Control 2	59±7	87±16	208±33	43±17	72±31	114±40	117±57	97±64	184±71
Manure	52±12	127±82	219±34	46±17	82±30	115±18	115±46	109±68	210±36
NPK	49±12	83±11	177±43	47±25	81±39	119±19	111±29	86±36	189±18

[a] Averages and standard deviations of values from three areas were shown.

Table 3-4. Yield of Nart farm from 2010 to 2013

					Crop yield in each plots and standard deviations [a]				
		Crops		Units	Control 1	Control 2	NPK	Manure	Statistical significance
2010	Area 1	Rye	(grain yield)	(Mg/ha)	1.69±0.26	1.83±0.32	1.31±0.46	1.40±0.66	NS [b]
	Area 2	Potato	(yield of tuber)	(Mg/ha)	5.14±0.34	6.59±0.95	5.97±0.68	6.96±2.28	NS
	Area 3	Turnip	(yield of root)	(Mg/ha)	No data	18.6±5.0 b	6.3±0.9 a	0.4±0.1 a	
2011	Area 1	Potato	(yield of tuber)	(Mg/ha)	17.7±4.2	25.8±3.4	23.6±3.5	21.4±3.8	NS
	Area 2	Rye	(grain yield)	(Mg/ha)	2.18±0.26 a	1.75±0.35 c	1.65±0.10 b	1.86±0.09 ab	
	Area 3	Pea	(yield of shoot)	(g/m^2)	27.7±3.0 a	40.8±4.5 b	37.3±3.6 b	42.3±1.1 b	
2012	Area 1	Rye	(grain yield)	(Mg/ha)	1.67±0.24	1.60±0.61	1.20±0.48	1.47±0.57	NS
	Area 2	Pea	(yield of shoot)		-	-	-	-	
	Area 3	Turnip	(yield of root)	(Mg/ha)	0.24±0.17	0.49±0.35	0.44±0.28	0.81±0.57	NS
2013	Area 1	Turnip	(yield of root)	(Mg/ha)	6.33±1.06	6.12±2.74	7.32±1.44	8.95±3.31	NS
	Area 2	Pea	(yield of shoot)	(Mg/ha)	20.8±3.0a	48.7±10.1ab	39.6±6.0ab	53.6±16.6b	
	Area 3	Potato	(yield of tuber)	(Mg/ha)	10.9±3.7a	17.7±1.2b	16.7±2.6ab	17.8±0.8b	

[a] Yield of the crops were calculated from the weight of edible parts of sampled plants from the 3.3 m^2 area in tested field, the average and standard deviation value of four replications were used in this table.

[b] NS means no significant difference between plots within lines, and values with the same letters within lines are not significantly different at $p<0.05$.

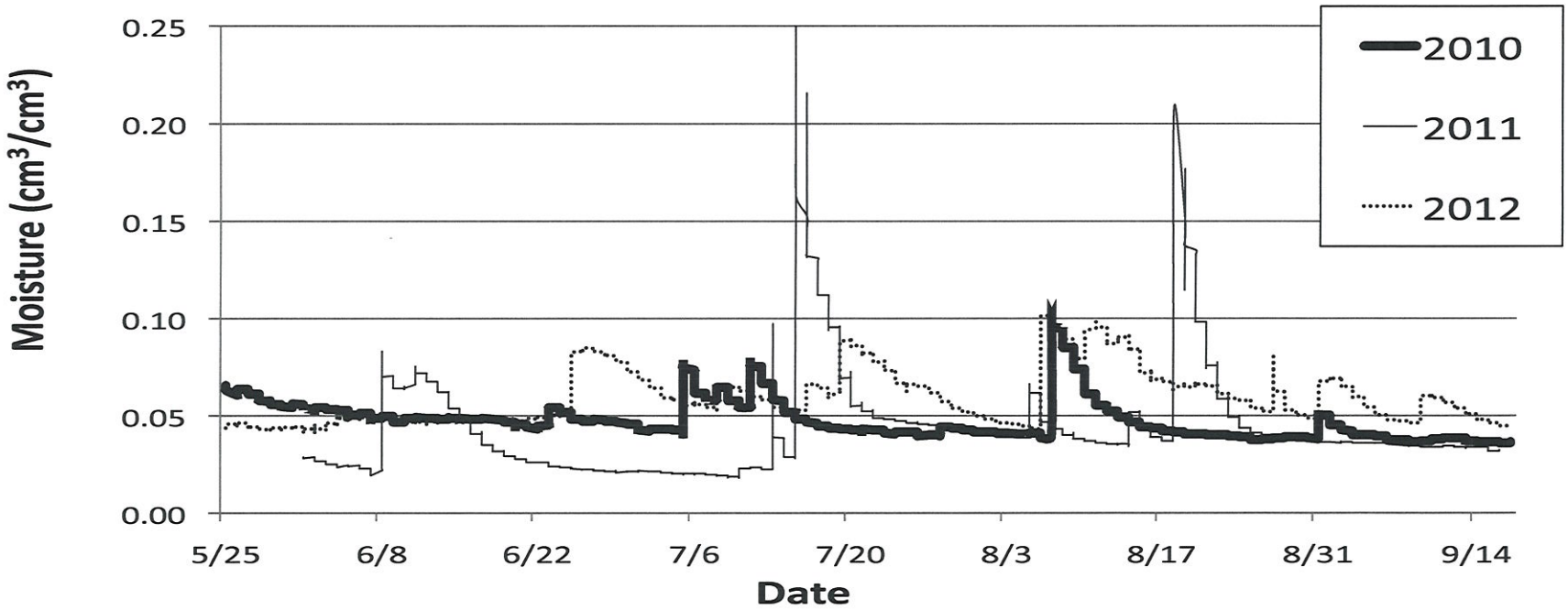


Figure 3-2. Changes in soil volumetric water content in experimental plot in Nart farm (2010-2012)

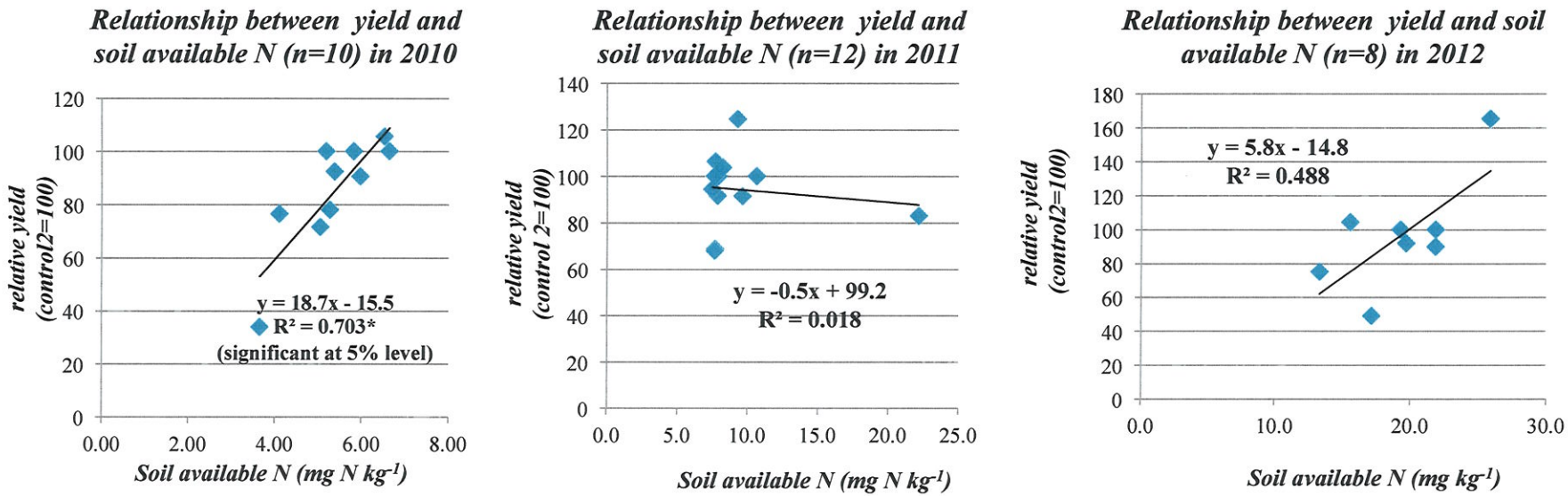


Figure 3-3. Relationships between relative yield [a] and soil available N in 2010 (a), 2011 (b), and 2012(c).

[a] Yield of the crops were calculated from the weight of edible parts of sampled plants from the 3.3 m^2 area in the tested field, the average of four replications were used in the figure.

* significant at 5% level

III. VI. Field experiment for appropriate use of animal manure in "Nart farm", Mongolia

III. VI. I. Introduction

In Mongolian, there are few a developed chemical and a heavy machinery industries. Also there are almost no use of animal manure, compost fertilizer and chemical fertilizer. However, in Mongolia, most of land has unpolluted (clean) environmental condition (air, soil and water). Therefore, most kinds of crops are growing in the ecologically pure environment. The rain fed and irrigated condition has been regarded as the most important resources to increase the crop production. Now farmers are using only less than 60% of total arable land for crop production because fallow treatment is needed to maintain the productivity. Last 5 to 10 years, any fertilizer use was less than 5% of total fertilizer for crop production. It would not be sufficient to maintain both of productivity and sustainability. On the other hand in Mongolia, there are many other considerable factors affecting on crop production, and one of the major factors is present climate change and the consequential drought. This cause soil erosion and desertification process in arable area. For Mongolian agriculture to disseminate and introduce the soil conservation technology for crop production, use of organic material is a part of solution. Amendment of animal manure and compost fertilizer is considered to be important key technology to prepare quality level for sustainable production. The positive effect of manure application to maintain the productivity of agricultural soil in Mongolia was shown in this study. However, practically, to determine the adequate amount and types of manure for Mongolian agriculture is the next issue. Therefore I tested the two types of manure, animal manure 2 year matured and 2 month matured for potato and wheat production. In this study, I also tested the effect of applied amount of both types of animal manure; the manures were applied as 20 Mg ha^{-1}, 40 Mg ha^{-1}, 60 Mg ha^{-1}, respectively.

III. VI. II. Materials and methods

Similar to the other experiment in this chapter, the field experiment was conducted in the Nart Experimental Farm of the Mongolian State University of Agriculture (48°36' 42.3" North, 106°29' 20, 7"East), and the soil of this field was classified according to the FAO-UNESCO classification system as a Kastanozem soil (FAO-UNESCO,1990). The field experiment was conducted in 2013. In this experiment, I used seven fertilization methods (plots) of manure using 2 years matured manure (2y-manure) and, 2 months matured manure (2m-manure) for potato and wheat cultivation in Mongolia. Both manure was made from goat and sheep dung. Seven plots were as follows; i) no fertilization (control), ii) application of 2m-manure 20 Mg ha^{-1}, iii) 2m-manure manure 40 Mg ha^{-1}, iv) 2m-manure 60 Mg ha^{-1}, v) 2y-manure 20 Mg ha^{-1}, vi) 2y-manure 40 Mg ha^{-1}, vii) 2y-manure 60 Mg ha^{-1}. Plot design was shown in figure 3-4. Manure was applied on May 30 in 2013. In the manure plot, I used manure made from sheeps and goats dung in Nart area around the Nart experimental farm. Potato was seeded on June 15 with the line interval of 70 cm, and plant interval of 30cm. Wheat was seeded on may 31 with the line interval of 15cm, and plant interval of 1 cm. To observe increase of yield of potato and wheat by the amount of animal manure application, crop yield was measured in September 2013. I measured potato and wheat yield after the harvest. Yield of the crops were calculated from the fresh weight of edible parts of samples from the four places in tested field.

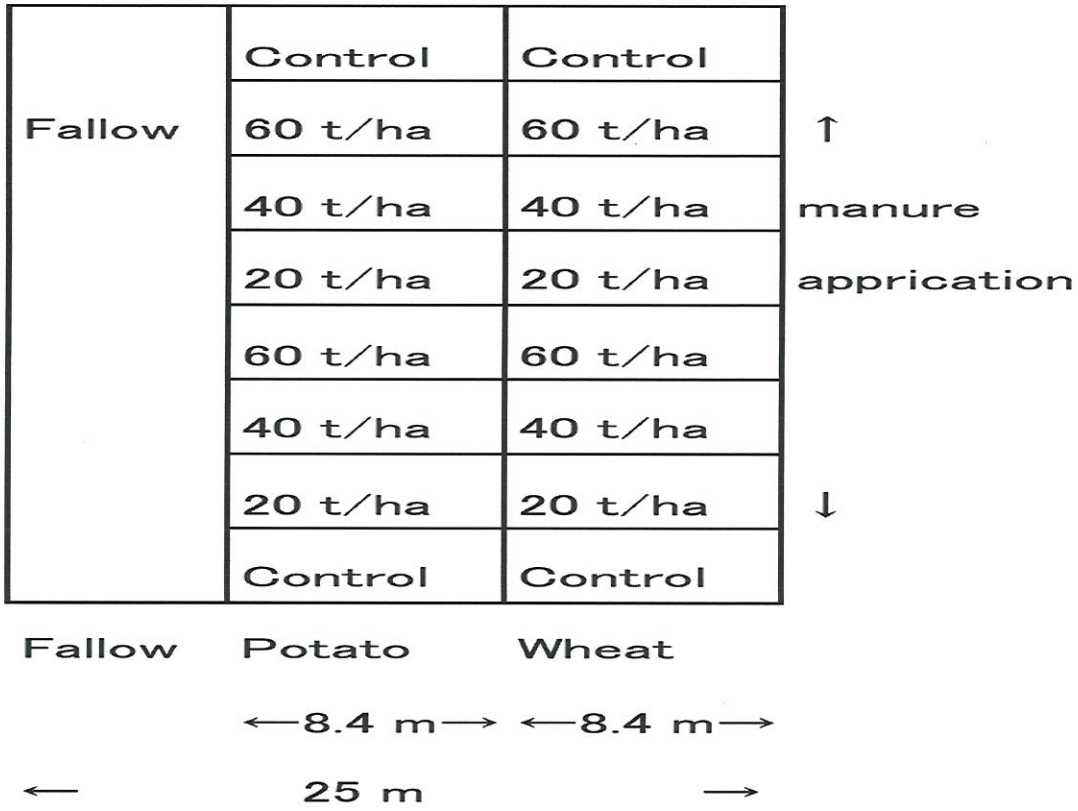


Figure 3-4. Plot design of the field experiment for determination of the effect of manure application amount on crop yield

III. VI. III. Results and discussion

III. VI. III. I. Crop yield in 2013

The potato yield in 2013 is shown in figure 3-5. When I compared the applications of 2y-matured and 2m-manure plots, 2y-manure applied plots had higher yield than 2m-manure applied plots. Significant higher yield was observed for 60 Mg ha^{-1} application of 2y-manure than control. Among 2y-manure applications, there was no significant difference between plots. The wheat yield in 2013 was shown in figure 3-6. For wheat yield, though no significant difference was observed between plots, the highest yield of wheat was observed for 20 Mg ha^{-1} application of 2m-manure. Figure 3-7 and 3-8 shows the relationship between crop yield and the amount of manure. Potato yield was positively related to the amount of both types of animal manure. For wheat yield, positive relationship was observed only for 2y-manure. These results indicated that both types of applied manure had positive effect on crop yield, but the greater effect was observed for 2y-manure than 2m-manure.

III. VI. III. II. Recommendation for manure application amount

Statistical significance between manure applied plot and control was observed only for potato yield, thus the recommendable manure use was discussed using the potato yield data. For potato yield, when considering the long time matured manure application, 20 Mg/ha^{-1} was regarded as sufficient level of the manure application. Long-time matured manure was considered to be better to maintain crop productivity, however, on the other hand, short time matured manure is convenient for annual use. Among plots with 2m-manure application, highest yield was observed for 40 Mg ha^{-1}. Significant positive effect of manure was observed for long-time (2 years) matured manure though 2m-manure seemed to be convenient for use. Thus, when we focused on 2m-manure, recommendable amount of 2m-manure was expected to be 40 Mg ha^{-1} in Mongolia. From these results, it was shown that long maturing time of manure and applied manure amount had positive effect on crop yield in Mongolia.

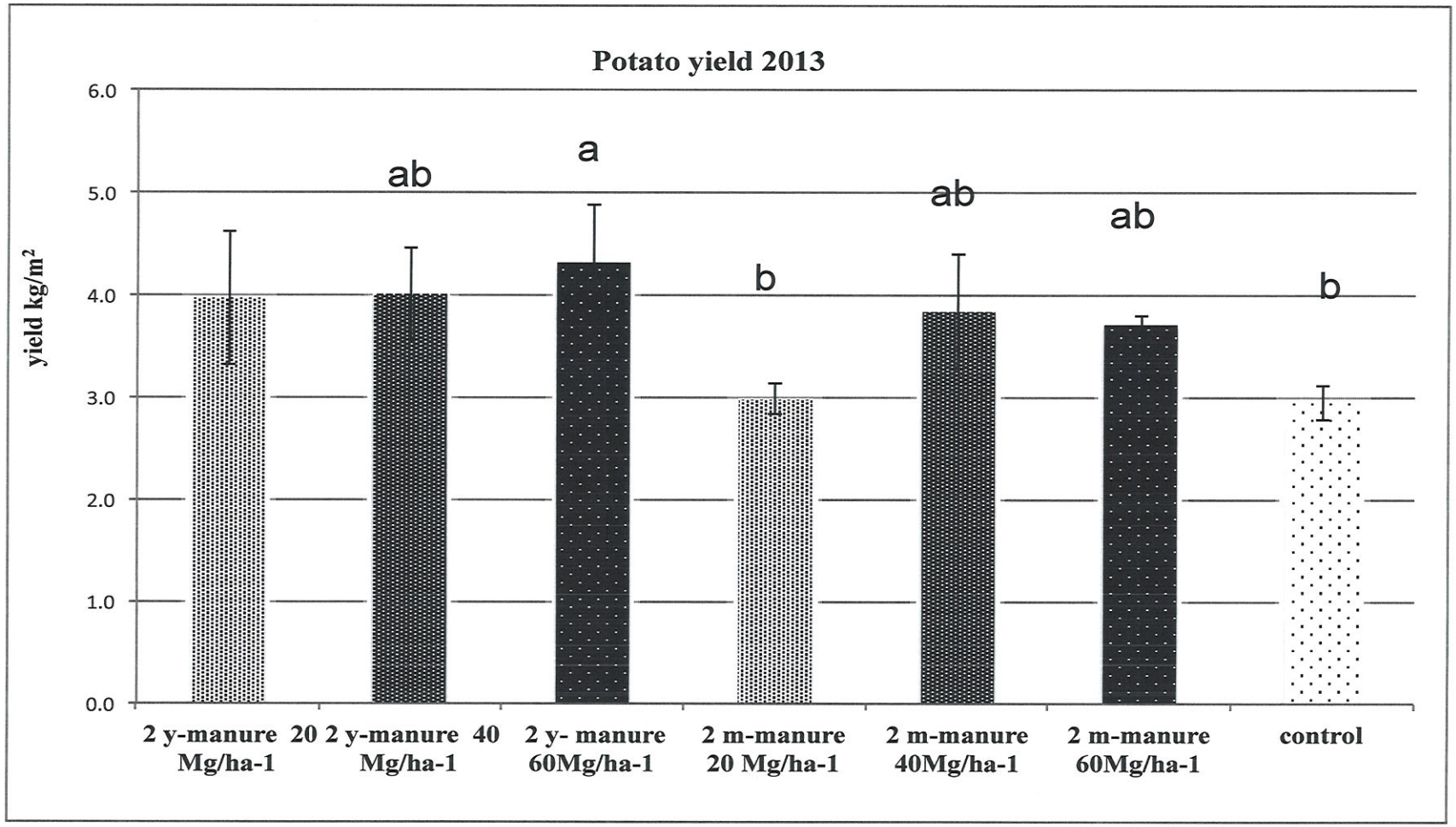


Figure 3-5.Values are the mean of three replicated values and the error bars indicates the standard deviation. Values followed by different letters were found to be significantly different (ANOVA; $P < 0.05$).

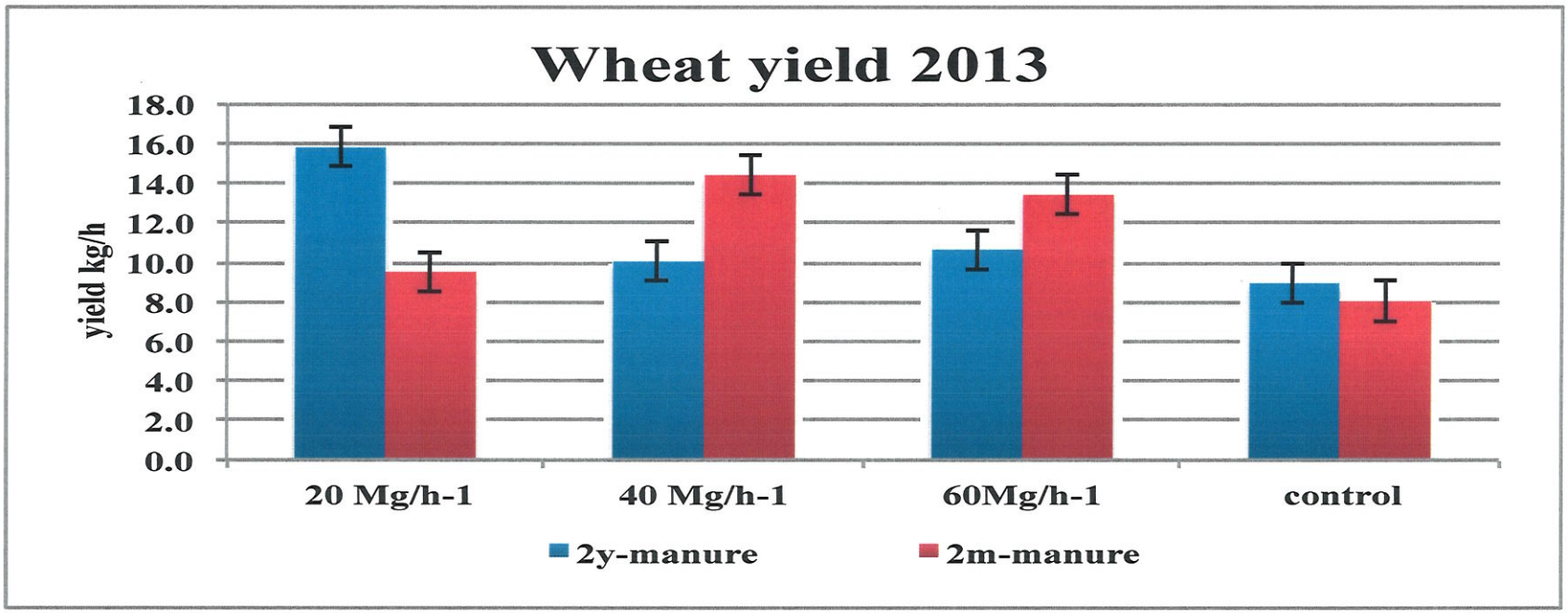
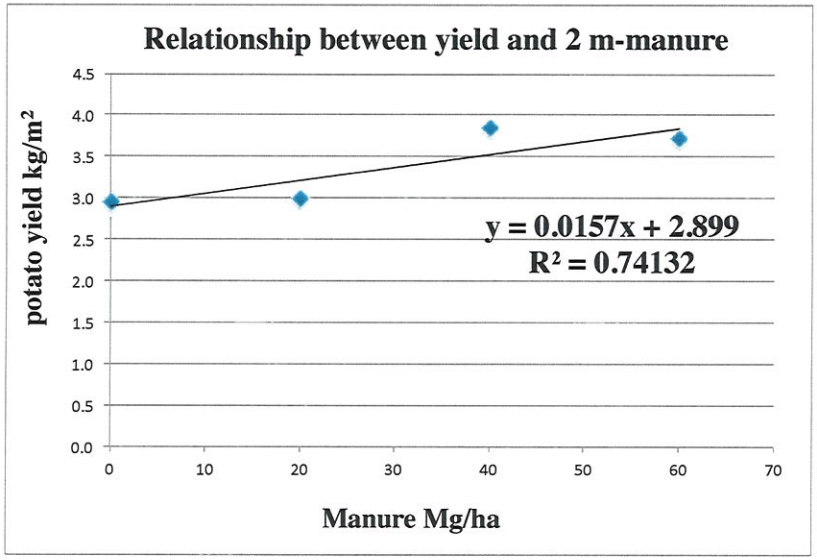


Figure 3-6. Values are the mean *of three replicated values and the error bars indicates the standard deviation



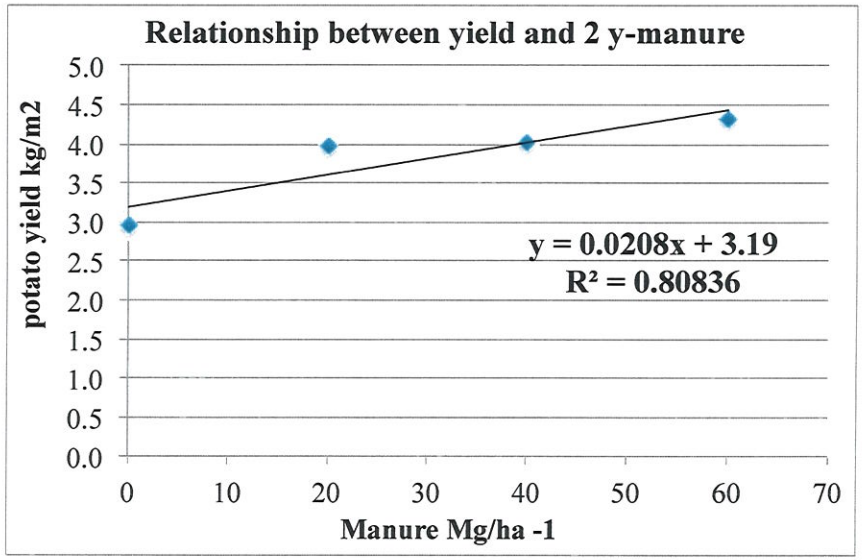
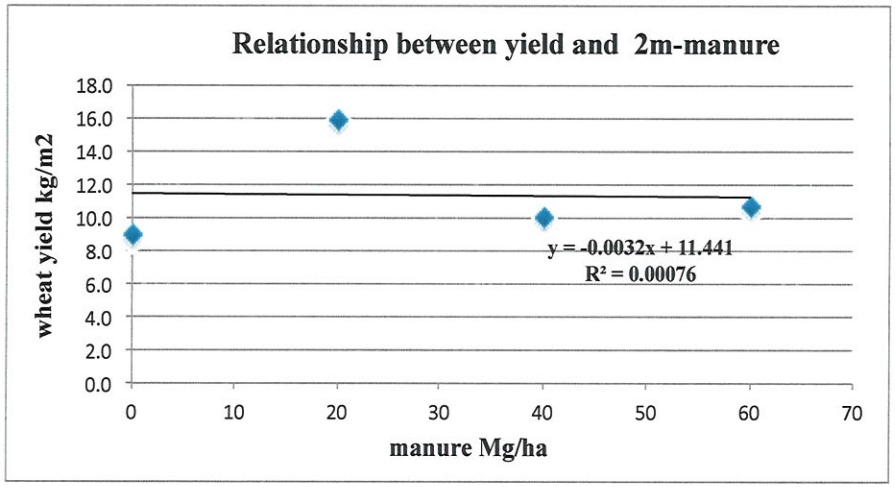


Figure 3-7. Relationships between relative potato yield and applied manure amount in 2013



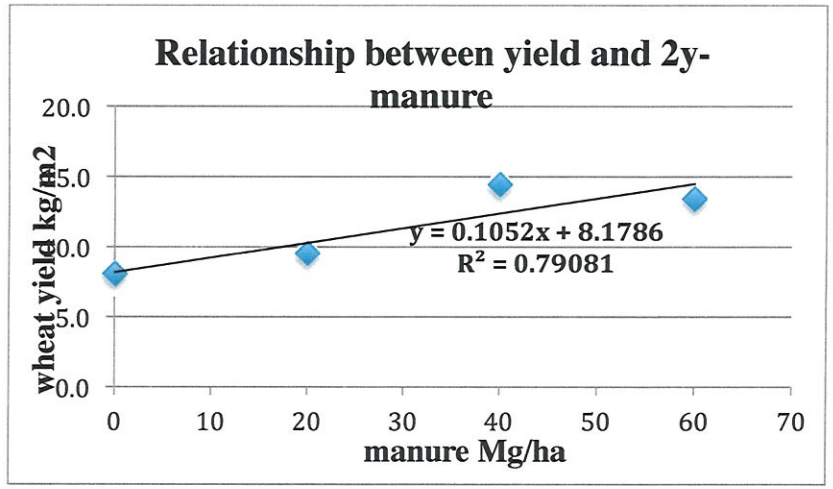


Figure 3-8. Relationships between wheat yield and applied manure amount in 2013

III.IV. Summary

Recently, soil degradation is becoming a very serious agricultural problem in Mongolia. As one approach to improve Mongolian agriculture, from 2010 to 2012, I introduced a crop rotation system and use of animal manure at the Nart Experiment Farm of the Mongolian State University of Agriculture. The crop rotation system was tested using potato (*Solanum tuberosum L.),* rye (*Selcate cereal L.*), turnip (*Brassica rapa L.var.glabra*) and pea (*Pisum sativum L.*).as green manure. In the field study, three fertilization patterns were used: i) no fertilization (control plots); ii) application of animal manure of 40 Mg $ha^{-1}y^{-1}$ (manure plot); and iii) application of chemical fertilizer of 90 kg N $ha^{-1}y^{-1}$, 90 kg P_2O_5 $ha^{-1}y^{-1}$ and 90 kg K_2O $ha^{-1}y^{-1}$ (NPK plot). In the manure plot, I used manure made from sheeps and goats dung in Nart area around the Nart experiment farm, because these animals are most common livestock in Mongolia. In the winter, dung of sheeps and goats were accumulated and naturally fermented for three month, and were used for the present study. The experimental field had been separated into three crop areas, and crops of the first, second and third years, respectively, were turnip-potato-rye (area 1), potato-rye-pea (area 2) and rye-pea-turnip (area 3). Each crop area also had two control plots. Crop yield and soil properties (pH(H_2O), CEC, available N (incubation method), available P (Truog method and Olsen method), and exchangeable K, Ca, Mg) were measured after the harvest each year. During the three years of this study, amount the soil properties, the effect of fertilization was observed only for the available N value, in 2012, which was the highest and tested to be higher for the manure plot (219 mg N kg^{-1}) than other plots (155-191 mg N kg^{-1}). No effect of chemical fertilizer was observed on soil properties. Yields were 5.1-38.8 Mg ha^{-1} (potato tuber), 1.3-2.2 Mg ha^{-1} (rye grain) and 0.4-18.6 Mg ha^{-1} (turnip root). Crop yields were positively related to soil available N value in 2010 and 2012. From these results, I considered that i) to increase the crop yield, amount of soil available N should be increased, ii) animal manure might increase the amount of soil available N and that was more favorable to soil productivity than chemical fertilizer applications. Add to this, small field experiment to test the effect of manure amount (20-60 Mg ha^{-1}) on potato and wheat yield was conducted using long-time (2years) matured manure and short-time (2 month) matured manure. As a result, only long-time matured manure increased crop yield significantly. In this experiment, there was no significant difference between 20 to 60 Mg $ha^{-1}$of manure application, therefore, for crop yield, application of 20 Mg $ha^{-1}$of long-time matured manure was expected to be recommendable application amount. Overall, it was shown that long maturing time of manure and applied manure amount had positive effect on crop yield in Mongolia.

Chapter IV. Speciation and bioavailability of Se in agricultural field

IV.I. Introduction

Selenium (Se) is known to have chemical properties in soils. Its chemical speciation can be controlled by pH and redox potential, and both of them are likely to be sorbed onto oxy-hydroxides of aluminum (Al), iron (Fe) or manganese (Mn) in soils. The average Se contents of world soil are 0.44 and 0.67 mg kg^{-1}, respectively (Kabata-Pendias, 2011). Se is major pollutants released from metal or mining and smelting sites (Crecelius et al. 1974; Lindsay and Spiers 2005; Ragaini et al. 1977). It have long been listed as priority pollutants by the US Environment Protection Agency (EPA) (Keith and Telliard 1979). Although Se is an essential element for animals, it is highly toxic and it can cause blind staggers in animals in areas with high Se contamination such as the Kesterson Reservoir drainage of the San Joaquin Valley in California (Ohlendorf, 1989). Selenium concentration in drain water from the Kesterson Reservoir averaged about 300 μg L^{-1} and amounts of Se in soils or sediments were reported up to 80 mg kg^{-1} (Fujii et al., 1988; Martens and Suarez, 1997). Like other contaminants, the amounts of Se in soils that are available to plants can be a main factor affecting their mobility in the food chain. For agricultural soils especially, there are important physico-chemical and biological differences of Se between non-flooded soil and wetland soils. Therefore, the quantitative data for predicting speciation of these trace elements in soils and the consequent transfer to plants under non-flooded and wetland conditions are needed. To understand Se availability, this chapter gives a summary of Se speciation and changes with pH and redox potential and their sorption agents in soils. Further, the sorption level and sorbed Se amounts for each sorption agent is discussed.

IV.II. Selenium speciation and bioavailability in non-flooded and wetland soils

IV.II. I. Se speciation and Eh-pH status

In the world soil environment, pH normally ranges from 4 to 9. Also, soil Eh fluctuates normally between -300 and +900 mV: aerated soils have an Eh over +400 mV; moderately reduced soils are between +100 and +400 mV; reduced soils are between −100 and +100 mV; and highly reduced soils are between −100 and −300 mV (Husson, 2013). Within these pH and Eh ranges, Se forms selenate (Se(VI)), selenite (Se(IV)), elemental Se (Se(0)), selenide (Se(-II)), and organic Se species in the soils (Kabata-Pendias, 2011). The pH-Eh diagram of Se in an aqueous system is shown in Fig. 4-1 (modified from Takeno, 2005). Using thermodynamic data, Elrashidi et al. (1987) reported that Se(VI) is the major species in a solution at high redox (pe + pH>15.0), Se(IV) species are predominant in the medium redox range (pe + pH <15.0 and >7.5), Se(-II) is the major species at low redox (pe + pH<7.5), and H_2Se^0 species contribute only under strongly acid conditions. Similar trends have been observed for most soils and sediments; for example, in the Hyco Reservoir sediment of North Carolina, Se(VI) was the predominant soluble Se species under the oxidized condition (Eh = 500 mV), Se(IV) was predominant for the Eh range from 0 to 200 mV, and elemental Se and metal selenides were predominant under more reduced conditions (Eh < -200 mV) (Masscheleyn et al., 1991). In the soil environment, the Se speciation can strongly affect Se mobility in soil environment. For the Se contaminated soil of the Kesterson Reservoir in the San Joaquin Valley, Fujii et al. (1988) reported the proportion of soluble Se ranged from 1 to 11%, and most of the soluble Se was Se (VI) while most of the adsorbed Se was Se (IV). In another study on Kesterson Reservoir sediment, Weres et al. (1989) reported that Se(0) was present as the dominant form in dry sediment because of its stability under oxidizing conditions. Using X-ray adsorption spectroscopy (XAS), Tokunaga et al. (1996) showed that Se in contaminated soil from the Kesterson Reservoir occurred primarily as the monoclinic elemental form, and was far less mobile than other forms. Also, they reported that the rapid re-oxidation of Se(0) to form a mixture of Se(IV) and Se(VI) within 2 days was observed, while Se in sediment including organic matter remained in the Se(0) state. For the elemental Se in Se enriched sediment from the San Joaquin Valley, Zawislanski et al. (2003) showed that the solubilization rate due to oxidation of Se(0) was anticipated to be very low (1-2% per year). From these findings, generally, it can be stated that Se mobility tends to be higher for the oxidized (or alkaline) conditions and lower for the reduced (or acidic) conditions.

IV.II.II. Se speciation and bioavailability in non-flooded soils

When considering non-flooded field soils, Se (VI) is the most available Se species to growing plants while Se (IV) is less available because of its high degree of adsorption onto soil particles (Lauchli, 1993; Terry et al., 2000; Zayed et al., 1998). In a pot study, Zhao et al (2005) showed that uptake of Se (VI) by *Brassica campestrris* was more than two times higher than that of Se (IV). Balistreiri and Chao (1987) reported that Se (IV) and phosphate were sorbed to similar extents on goethite. However, under an acidic soil environment, Se(VI) was unstable and leached easily (Neal et al., 1987a, 1987b). Therefore, Se(IV) was considered to be the major Se form in acid soils (Asagawa et al., 1977). Besides, Yamada et al. (1998) reported that the major part of 0.1 M NaOH extractable Se for Japanese soils was Se (IV), and its solubility was lower than that of Se(VI). The primary adsorption mechanism of both Se(IV) (Neal et al., 1987a, 1987b) and Se(VI) (Neal and Sposito, 1989) has been regarded as ligand-exchange. Adsorption of Se (VI) has been reported for goethite and many kinds of Fe oxy-hydroxides (Hington et al., 1974; Parida et al., 1997; Rashid et al., 2002), Mn oxides (Saeki et al., 1995) and Al oxides such as gibbsite or allophane mineral (Neal et al., 1987a, 1987b; Parfitt, 1978; Rajan, 1979; Rajan and Watkinson, 1976). Peak and Sparks (2002) studied the adsorption mechanism of Se (VI) onto Fe oxides and hydroxides using X-ray adsorption fine structure (XAFS), and they showed that Se(VI) formed only an inner-sphere complex on hematite but formed a mixture of outer-sphere and inner-sphere complexes on goethite and hydrous ferric oxide; further, the importance of the inner-sphere complex decreased with increasing pH from 3.5 to 6.0. This would explain the lower sorption strength of Se(VI) than Se(IV) in soils (Rashid et al., 2002). A radioactive tracer study using ^{75}Se added as selenite solution to Japanese soils showed that 80-100% of added ^{75}Se tracer was adsorbed by oxy-hydroxides of Al or Fe (Nakamaru et al., 2005). Relationships between Se and soil oxy-hydroxides of Al or Fe were also reported for New Zealand soils (Jhon et al., 1973) and Canadian soils (Levesque, 1974a, 1974b). The oxy-hydroxides of Al or the Fe adsorbed Se fraction was regarded as plant available Se in acidic non-flooded soil. Zhao et al. (2005) suggested that the soil Se extracted with 1 M KH_2PO_4 highly correlated with plant Se uptake. For instance, phosphate solution has been used in many studies to extract the soil adsorbed Se (Balistreieri and Chao, 1987; Dhillon and Dhillon, 1999; Martens and Suarez, 1997; Stroud et al., 2012; Zawislanski et al., 2003). Another study indicated that

the phosphate ion inhibited the SeO_3^{2-} sorption as a competitor for the ligand-exchange reaction in Japanese soils (Nakamaru et al., 2006a). In this study, the soil-soil solution distribution coefficient (K_d) of ^{75}Se decreased with the addition of 0.1mmol l^{-1} HPO_4^{2-} under the solution pH condition of 6.2 to 7.3 as shown in Fig. 4-2. Under high pH condition (that is, in alkaline soil), sulfate was also seen to be a chemical analogue of Se (VI), and Se solubility was enhanced by sulfate (Brown and Carter, 1969). However, such an exchange of Se by sulfate was not found to be significant for acid Japanese soils (Nakamaru and Sekine, 2008).

IV.II.III. Se speciation and bioavailability in wetland soils

It is generally agreed that under oxidized and moderately reduced conditions Se solubility is governed by an adsorption-type mechanism rather than by precipitation and dissolution reactions (Masscheleyn and Patrick, 1993). However, under wetland conditions, Se (VI) can be reduced to Se (IV), and then Se (IV) also can be reduced to Se(0) (Yamada et al., 1999; He et al., 2010). It was reported that Se (VI) in soil solution was reduced to Se (IV) and Se(0) after 6 to 10 weeks under a flooding condition, and the reduction decreased to the uptake availability rice plants to Se (Mikkelson et al., 1989). Forming of Se(0) or metal selenide at low redox potential can limit Se solubility (Masscheleyn and Patrick, 1993). With respect to wetland Se biogeochemistry, it can be expected that the organic matter-bound Se plays an important role. For the Se fraction in the wetland system of the Benton Lake National Wildlife Refuge in Montana, Zhang and Moore (1996) reported that Se(0) and organic matter-bound Se percentages were 46% and 33%, of total Se, respectively, while oxide-bound Se was less than 4% of total Se. Chen et al. (2010) reported that the major form of Se in paddy soil was organic-sulfide matter-bound Se and Se(0), which accounted for more than 50% of the total Se. Wang et al. (2012) also suggested that while Fe and Mn oxide-bound Se was the dominant fraction in Chinese non-flooded soil, organic matter-bound Se accounted for most of the total Se in paddy soil, and the contribution of organic matter-bound Se for Se uptaken by corn plants was dominant over the Fe and Mn oxide-bound fraction. Further, due to the reduction of Fe and Mn oxides, the relative strength of Se adsorption on Fe and Mn oxides should be lower under the flooded condition (Wan et al., 2013). Zawislanski et al. (2001) reported a strong correlation between Se and C for suspended particulate matter of wetlands in the San Francisco Bay of California; this result suggested the importance of organic particulate deposition of Se on Se concentration in the solution phase. Although the sorption mechanism of Se onto organic matter has not been studied in detail, Kamei-Ishikawa et al. (2008) reported that Se sorption onto humic acid followed the Freundlich isotherm. It is obvious that organic matter can affect Se availability to plants; however, the release rate of Se from organic matter and the quantitative evaluation of bioavailability of organic matter-bound Se are needed for prediction of Se bioavailability in wetland systems.

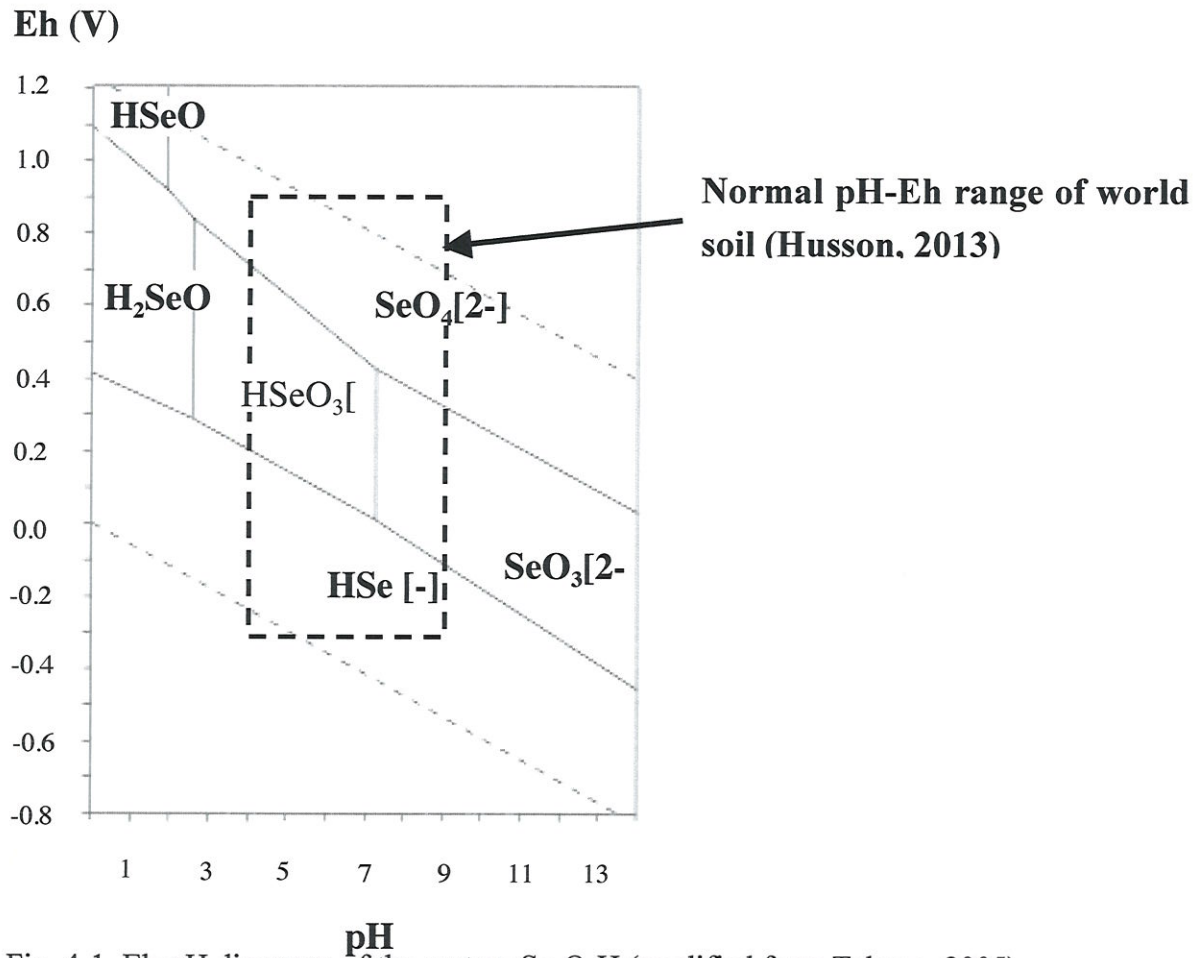


Fig. 4-1. Eh-pH diagrams of the system Se-O-H (modified from Takeno, 2005).

The present Eh-pH diagram was acquired under Sb concentration level of 10^{-10} mole/kg and normal pressure (10^5 Pa). The thermodynamic database used for this figure is SUPCRT92 (Johnson et al., 1992) with 98 updates distributed by Everett Shock from his website on the Internet (http://chemistry.asu.edu/faculty/shock.asp).

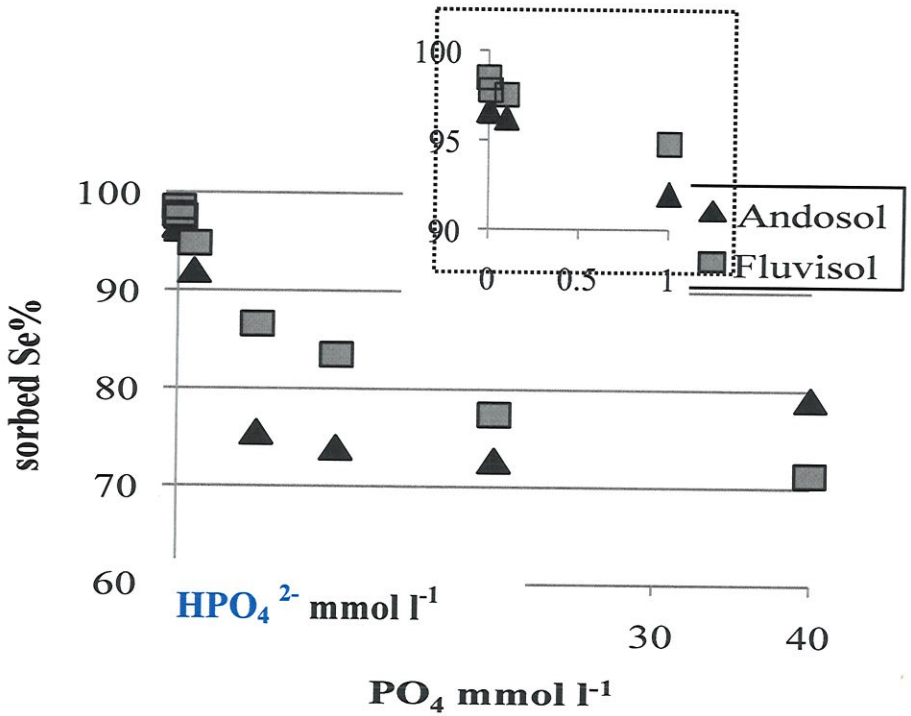


Fig. 4-2. The changes of the sorbed Se % values of Andosol and Fluvisol plotted against the phosphate concentration in the soil solution under elevated levels of PO_4 concentration with Na_2HPO_4/KH_2PO_4 (Soil solution pH range was 6.2 to 7.0) (modified from Nakamaru et al., 2006a).

IV.III. Summary

Studies on the sorption behaviors of selenium (Se) is reviewed. Se chemical speciation can be controlled by pH and redox potential, and both of them are likely to be sorbed onto oxy-hydroxides of aluminum, iron or manganese on soils. For agricultural soils especially, there are important physico-chemical and biological defferences between non-flooded and wetland soils. Se forms Se (IV), Se(VI), Se(0), Se (-II), and organic Se species at soil pH and redox conditions. Under non-flooded conditions Se solubility is governed by an adsorption mechanism onto metal oxy-hydroxides rather than by precipitation and dissolution reactions; however, for the conditions of wetland soils, it can be expected that Se (0) and organic matter- bound Se play an important role.

Chapter V. Effect of long-term phosphorus fertilization on soil Se uptake by crops in northern Japan

IV.I. Introduction

In most soils, selenium (Se) is a naturally occurring trace element. Although Se is an essential nutrient for animals, it can also be toxic to them when it occurs at high concentrations in soil, water, and plants (Ohlendorf, 1989). Thus, Se has been listed as a priority pollutant by the US Environment Protection Agency (US EPA) (Keith and Telliard, 1979) and much attention has been paid to its biogeochemistry and behavior in the environment. Numerous studies have shown that application of Se to soil can promote plant growth by increasing the activity of antioxidant enzymes (Djanaguriannman et al., 2005). The Se content of crops has received considerable attention in recent years because of its importance in the food chain and because of its effects, both beneficial and harmful, on plants and animals. Meanwhile, it is known that fertilizers may contain trace element contaminants such as cadmium or uranium that can be inadvertently introduced into soils (Mortvedt, 1996; Takeda et al., 2005). In particular, phosphorus (P) fertilizer, applied over the long-term, can serve as an important source of trace elements such as arsenic, cadmium and lead that can potentially accumulate in plants and soils. Se is also found in P fertilizer (0.5-25 mg Se kg^{-1} P fertilizer, He et al., 2004). The behavior of these trace elements is influenced substantially by soil management (Jiao et al., 2013). In Japan, most agricultural land has high levels of P due to excessive use of P fertilizer (Mishima et al., 2010). Therefore, it is speculated that P fertilization is a factor controlling Se uptake in crops. In upland soils, Se forms selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) (Lauchli, 1993; Terry et al., 2000; Zayed et al., 1998). However, in acidic soil, selenate is unstable and easily leached (Neal et al., 1987a, 1987b). Thus, selenite is considered to be the primary Se form in acidic soils (Asagawa et al., 1977). Yamada et al. (1998) reported that the major component of NaOH-extractable Se in Japanese soils was selenite, which has a lower solubility than selenate. A radioactive tracer study using ^{75}Se added to Japanese soils showed that 80-100% of added ^{75}Se tracer with selenite form carrier was adsorbed to oxy-hydroxides of Al or Fe as ligand-exchangeable forms (Nakamaru et al., 2005). As such, it has been suggested that, (i) Se can accumulate in acidic upland soils as ligand-exchangeable selenite as a result of P fertilization and (ii) that this ligand-exchangeable Se is available to plants given that it can be exchanged by phosphate ions (Dhillon and Dhillon, 1999; Zhao et al., 2005; Nakamaru et al., 2006). Though many studies suggest that P fertilizer can increase Se uptake by crops, little is known regarding the influence of P fertilization on Se behavior in field soil. The purpose of this chapter is to determine the effect of long-term P fertilization on soil Se and transfer of Se to crops in agricultural fields.

V.II. Materials and methods

V.II.I. Study area

In order to study the effect of P fertilization on major and trace elements in plants and soils, a field experiment was conducted in the northern area of Japan (Abashiri, Hokkaido Prefecture, 44.0° North, 144.2° East). The experiment was conducted from May 2009 to November 2011. Evaluation of soil Se and plant Se was started in 2010. Two fields were used in the study: one in the Urashibetsu area (U-A field) and the other in the Yasaka area (Y-C field). The soils of these two fields are classified according to the FAO-UNESCO classification system (FAO-UNESCO, 1990) as an Andosol and a Cambisol field, respectively. These two soil types are typical in upland fields in northern Japan. The two areas were chosen due to substantial differences in their available P levels. The Y-C field had been cultivated since 1925, while the U-A field was converted from forest land starting in 1983. Consequently, the U-A field had relatively lower available P content than the Y-C field, which had experienced long-term P fertilization.

V.III.II. Field experiment

Consistent with the major crop rotation used in the study area, in the field experiment, sugar beet (*Beta vulgaris* ssp. *vulgaris*), potato (*Solanum tuberosum* L.), winter wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.) were cultivated. To evaluate the effect of fertilization on soils and plants, four fertilization methods (in separate plots) were used: i)conventional NPK application (NPK), ii) P fertilization at half the conventional rate (P1/2), iii)no P fertilization (-P), and iv)no P and no K (-P-K). The fertilization methods constituting the experimental treatments and crop rotation system are summarized in Table 5-1. These four treatments were applied as four replicates in a randomized block design, resulting in a total of 16 experimental plots each in both U-A and Y-C fields. Nitrogen (N) was added as Chilean saltpeter for sugar beet and as ammonium sulfate for the other crops. P and K were added as superphosphate and potassium chloride, respectively. The Se content of N and K fertilizers was below than detection limit (0.5μg Se kg^{-1}>). The Se input at the two field sites resulting from P fertilization is also shown in Table 5-1. The mean annual P and Se input due to chemical fertilizer were 80.7 kg P ha^{-1} $year^{-1}$ and 452 mg Se ha^{-1} $year^{-1}$, respectively. The level of P input was set equal to the mean P input in upland fields in Japan. According to Mishima et al. (2010), while mean P input to Japanese upland fields

declined from 124.1 kg P ha^{-1} $year^{-1}$ in 1985 to 83.6 kg P ha^{-1} $year^{-1}$ in 2005, the fertilization level is still high. I assume that the level of Se input observed in this study is equal to the level normally occurring in Japan. Soil samples taken from a depth of 0 to 20 cm were collected from each of the 16 plots in both field sites; soil sampling was done in late spring or early summer after sowing (May or June) in 2010 and 2011.

V.III.III. Analysis of soil and plant samples

For soil samples, the amount of available P, total P, total Se and soluble Se amount were measured in 2010 and 2011. The available soil P was extracted by the Truog method using a pH 4 $(NH4)_2SO_4$ ˙ H_2SO_4 solution (Truog, 1930, modified by Blakemore et al., 1981). We chose this method because it is the method that is most commonly used for evaluation of available soil P in Japan. Exchangeable K amount was determined by the Schollenberger method (Schollenberger and Simon, 1945). The P adsorption coefficient (mg P_2O_5 adsorbed to 100g of soil) was determined by adding 50 ml of a 2.5% $(NH_4)_2HPO_4$ solution to 25 g of air dried soil, shaking the resulting suspension for 24 h, and then measuring the P concentration of the solution. Soil Se was measured by Atomic Absorption Spectrometry (Thermo Fisher, iCE 3000) and a hydride generation system (Thermo Fisher, HYD-10) following digestion of the sample with $HClO_4$-HNO_3-HF. Plant samples were digested using a similar method, and Se concentration was determined by ICP-MS (Yokogawa Analytical Systems, Agilent 7500c). Plant Se uptake was determined by multiplying the Se concentration and the dry weight of plant. Soluble Se of the soil samples was also measured following the method proposed by Yamada et al. (1990), involving extraction with hot water (90°C) added to the soil in a 10 to 1 ratio (water:soil ratio) and shaking for 30 min.

A soil-plant transfer factor (TF) for Se was calculated using the following equation based on the measured Se content of the soil and plant samples according to Uchida et al. (2007):

TF = Concentration of Se in plant/Concentration of Se in soil.

Table 5-1. Crop rotation system and fertilizer (kg/ha) regimen for the two field sites used in the experiment from 2009 to 2011

	2009			2010			2011			Total P input	Total Se input [a]
	N	P	K	N	P	K	N	P	K	kg P ha^{-1}	mg Se ha^{-1}
U-A field site	Sugar beet			Potato			Winter wheat				
NPK	160	109	133	100	79	108	100	65	83	253	1418
P 1/2	160	55	133	100	39	108	100	33	83	127	709
-P	160	0	133	100	0	108	100	0	83	0	0
-P-K	160	0	0	100	0	0	100	0	0	0	0
Y-C field site	Sugar beet			Potato			Barley				
NPK	160	109	133	100	79	108	60	44	66	231	1296
P 1/2	160	55	133	100	39	108	60	22	66	116	648
-P	160	0	133	100	0	108	60	0	66	0	0
-P-K	160	0	0	100	0	0	60	0	0	0	0

[a] Se input was calculated based on Se concentration in P fertilizer of 0.44 mg Se kg^{-1}.

V.IV. Results and discussion

V.IV.I. Soil chemical properties in two field sites

Table 5-2 lists soil chemical properties of the two field sites. Soils in both fields were found to be acidic and both exhibited high phosphate adsorption coefficients (1164-1351 mg P_2O_5 adsorbed to 100g of soil) in the Ap horizon. Thus, it was assumed that, similar to the case of phosphate adsorption, the Se added to the soil along with P fertilizer could be readily adsorbed to Al or Fe oxyhydroxides as a ligand-exchangeable species. Most agricultural soils in the Abashiri area contain higher levels of available P than that recommended by Hokkaido Prefecture (44-131 mg P kg^{-1}) (Yoshida et al., 2005). Soil at the Y-C field site had higher available P than at the U-A field site, ranging from 400 to 700 mg kg^{-1} at the former site and from 200 to 300 mg kg^{-1} at the latter (Table 5-2). The P adsorption coefficients at both field sites were essentially the same, and available soil P of the unfertilized layer (40-80 cm depth) was greater at the U-A field site than the Y-C field site. As such, it was concluded that the higher available P of soil at the Y-C field site was due to the continuous input of P fertilizer. The change in available soil P and total P content as a result of input of P fertilizer over the three periods of the experiment is shown in Table 5-3. Pooling the data from both sampling dates, I see that the range of available soil P in surface soil at the U-A field site increased from 83-99 mg P kg^{-1} in plots receiving no P fertilizer to 121-186 mg P kg^{-1} in plots receiving P fertilizer. Similarly, at the Y-C field site, available soil P increased from 194-257 mg P kg^{-1} in plots receiving no P fertilizer to 209-329 mg P kg^{-1} as a result of three years of continuous P fertilization. Available soil P and total P were found to be highest among those plots receiving NPK fertilizer, which is not surprising given that the NPK treatment constituted the highest P input.

V.IV.II. Se content of soils

Table 5-4 shows the total Se content of soil in 2010 and 2011. Se concentration in soils worldwide is reported to range from 0.005 to 1.9 mg Se kg^{-1}, with the mean concentration being 0.44 mg Se kg^{-1} (Kabata-Pendias, 2011). Yamada et al. (2009) reported that the Se content of Japanese soils ranges from 0.25 to 2.8 mg Se kg^{-1} in Andosols and from 0.14 to 1.04 mg Se kg^{-1} in Cambisols. The Se concentrations of the soils examined in this study fell within these ranges. At the U-A field site, soil Se content tended to be higher in the NPK-fertilized plots (0.51 to 0.63 mg Se kg^{-1}) and to

be lower in the -P, and -P-K plots (0.43 to 0.51 mg Se kg^{-1}). It was believed that the increase in Se content of NPK-fertilized plots is due to the input of P fertilizer. In contrast, at the Y-C field site, no such trend was observed, and the Se content of soil ranged from 0.57 to 0.65 mg Se kg^{-1} in 2010 and 2011 for all plots, regardless of fertilizer treatment. From these results, it is suggested that soil Se may increase as a result of continuous P fertilization. However, the effect of three years of P fertilization on total soil Se content, particularly in fields that have received long-term, continuous P input, is not clear. At both field sites, soluble Se in soils ranged from 0.007-0.009 mg Se kg^{-1} and did not appear to differ by fertilization treatment. Considering the mass-balance of Se in soils and fertilizers, the Se content of the fertilizer used in this study (0.44 mg Se kg^{-1}) would have been insufficient to increase soil Se significantly. In the NPK-fertilized plots, annual Se input to the surface soil (0-10 cm) was only 0.0005 mg Sekg^{-1} (calculated based on an assumed soil bulk density of 0.9 g cm^{-3}). I think that NPK fertilization in the Y-C field also increased soil Se, however, it was not statistically significant because soil Se content in the Y-C field was basically higher even in the no P fertilization plots. The Se content of soils at the Y-C field site was significantly higher than that at the U-A field site. Furthermore, Se content of soils was significantly correlated with available soil P, although no similar correlation was observed with total P content (Figure 5-1). The high level of available soil P content at the Y-C field site is assumed to be the result of long-term P fertilization, given that the Y-C field site has been used for agriculture since 1925. The U-A field site, in contrast, was converted to agricultural use only in 1983. These results indicate that Se content of soils at the Y-C field site was enhanced as a result of the long-term P fertilization in the area.

V.IV.III. Se concentration of plant shoots and Se uptake by crops

Shoot biomass was observed to differ by field site, with higher biomass of potato shoots being observed at the U-A field site (5000-5680 kg ha^{-1}) than at the Y-C field site (3610-4180 kg ha^{-1}) and barley shoot biomass (Y-C field site, 4970-6330 kg ha^{-1}) being greater than wheat biomass (U-A field site, 2551-3540 kg ha^{-1}). However, at both field sites and in both years, no differences among fertilizer treatments were observed for the yield of potato tuber, wheat grain and barley grain, and the shoot biomass of wheat and barley (data not shown). Table 5-5 shows the Se concentration and uptake by plants at both field sites. The Se concentration of potato tubers as well as wheat or barley grain was below the detection limit (< 0.5 μg Se kg^{-1}). Wheat and barley shoots had higher Se

concentration (20 to 28 μg Se kg^{-1}) than potato shoots (1.1 to 1.6 μg Se kg^{-1}). At the U-A field site, although the mean Se concentration of potato (2010) and wheat (2011) shoots was observed to be higher in plots receiving NPK fertilizer, the difference was not statistically significant. At the Y-C field site, no significant differences were observed among fertilizer treatments in terms of Se concentration of potato and barley shoots. However, with regard to a comparison of the two field sites, the Se concentration of potato shoots was found to be significantly higher at the Y-C field site than at the U-A field site in 2010. The Se concentration of wheat and barley shoots was essentially the same at both the U-A and Y-C field sites. The total Se inputs at the U-A and Y-C field site as a result of three years of P fertilization were 1418 and 1296 mg Se ha^{-1}, respectively (Table 5-1). In both cases, the values were sufficient to explain the Se uptake by plants at both field sites in 2011 (66 and 134 mg Se ha^{-1}, Table 5-5). However, no significant difference among fertilizer treatments was observed for Se uptake by potato, wheat, and barley at both field sites and in both years. In 2010, Se uptake by potato shoots was observed to be nominally higher at the Y-C field site than at the U-A field site, although the difference was not found to be significant. In 2011, Se uptake by barley at the Y-C field site was found to be significantly higher than Se uptake by wheat at the U-A field site. This is believed to be due to the higher Se concentration and biomass of barley shoots at the Y-C fields. These results indicate that the Se concentration of plants did not increase significantly as a result of three years of P fertilization. That said, similar to the case of soil Se concentration, the Se concentration of plant shoots at the Y-C field site was higher than at the U-A field site. In addition, plant Se uptake tended to be higher at the Y-C field site than at the U-A field site.

Table 5-2. Properties of soils at the field sites used in this study

	pH [a] (H_2O)	Available P [a] (mg P kg^{-1})	Exchangeable K [a] (mg K kg^{-1})	Phosphate adsorption coefficient [a] (mg P_2O_5 sorbed to 100g of soil)	Bulk density [a] (g cm^{-3})
Soil depth (horizon)					
U-A field site (Andosol)					
0-20 cm (Ap1)	**6.5**	**84.2**	**975.0**	**1351**	**0.90**
20-40 cm (Ap2)	**6.2**	**88.2**	**1161**	**1329**	**1.13**
40-60 cm (B1)	**6.2**	**43.6**	**1032**	**1338**	**1.18**
60-80 cm (B2)	**6.3**	**5.70**	**511**	**752**	**1.21**
Y-C field site (Cambisol)					
0-20 cm (Ap1)	**6.9**	**235**	**386**	**1233**	**0.92**
20-40 cm (Ap2)	**6.7**	**212**	**373**	**1164**	**1.02**
40-60 cm (B1)	**6.5**	**2.20**	**120**	**784**	**1.55**
60-80 cm (B2)	**6.5**	**3.10**	**149**	**669**	**1.60**

[a] Results are for plots at each field site receiving the -P-K fertilizer treatment in June 2009.

Table 5-3. Available soil P and total soil P of soils at the two field sites in 2010 and 2011.

Fertilizer Treatment	P content of soil (0-20 cm) (mg P kg^{-1})							
	U-A Potato 2010.5.25				U-A Wheat 2011.5.16			
	Available P		Total P		Available P		Total P	
	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]
NPK	186	62	19000	3100	129	20	19300	1900
P 1/2	160	51	20900	800	121	25	20400	3200
-P	99	16	18100	700	91	30	19700	1800
-P-K	98	9	17200	900	83	34	18200	3000
	Y-C Potato 2010.5.25				Y-C Barley 2011.6.2			
	Available P		Total P		Available P		Total P	
	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]
NPK	329	103	20400	2300	209	20	20600	700
P 2/1	294	65	19100	500	229	70	19400	1100
-P	257	33	19000	900	194	24	19300	1400
-P-K	264	8	19400	800	196	18	17700	3200

[a] Values are the mean of two replications and SD is the standard deviation.

Table 5-4. Se content of soils at the two field sites in 2010 and 2011

	Se content in soil (mg kg^{-1})											
	U-A Potato 2010.5.25				U-A Wheat 2011.5.16				Mean of U-A field and Y-C field [c]			
	Total Se		Soluble Se		Total Se		Soluble Se		Total Se		Soluble Se	
Fertilizer treatment	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]	U-A field [c]	SD [c]	U-A field [c]	SD [c]
NPK	0.63	0.12	0.009	0.002	0.51	0.04	0.009	0.001	0.50a [c]	0.06	0.009	0.0005
P 1/2	0.54	0.08	0.009	0.002	0.48	0	0.009	0.04				
-P	0.48	0	0.009	0.002	0.43	0	0.008	0.04				
-P-K	0.51	0.04	0.008	0.002	0.45	0.04	0.008	0.001				
	NS [b]		NS [b]		NS [b]		NS [b]					
	Y-C Potato 2010.5.25				Y-C Barley 2011.6.2							
	Total Se		Soluble Se		Total Se		Soluble Se					
	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]	Mean [a]	SD [a]	Y-C field [c]	SD [c]	Y-C field [c]	SD [c]
NPK	0.65	0.08	0.008	0.001	0.63	0.04	0.008	0.001	0.62b [c]	0.03	0.008	0.0006
P 1/2	0.6	0	0.008	0.001	0.6	0	0.007	0.001				
-P	0.57	0.04	0.009	0.001	0.63	0.04	0.008	0.001				
-P-K	0.65	0	0.008	0.001	0.63	0.04	0.007	0.001				
	NS [b]		NS [b]		NS [b]		NS [b]				NS [c]	

[a] Values are the mean of two replications and SD is the standard deviation.

[b] NS = no significant difference among four fertilizer treatments within each column (ANOVA test, $P<0.05$).

[c] Values are the mean and standard deviation of values for all fertilizer treatments and sampling depths at each field site. NS means no significant difference between the two field sites Values followed by different letters were found to be significantly different (ANOVA; $P<0.05$).

Table 5-5. Plant Se concentration and uptake in 2010 and 2011

Se concentration in plant shoots (mg Se ha-1)								
	2010				2011			
	U-A (Potato)		U-A total		U-A (Wheat)		U-A total	
Fertilizer treatment	Mean [a]	SD [a]	Mean [c]	SD [c]	Mean [a]	SD [a]	Mean [c]	SD [c]
NPK	0.0013	0.0002	0.0012a [c]	0.0001	0.028	0.005	0.023	0.003
P1/2	0.0011	0.0003			0.023	0.005		
-P	0.0011	0.0001			0.02	0		
-P-K	0.0012	0.0002			0.023	0.005		
	NS [b]				NS [b]			
	Y-C (Potato)		Y-C total		Y-C (Barley)		Y-C total	
	Mean [a]	SD [a]	Mean [c]	SD [c]	Mean [a]	SD [a]	Mean [c]	SD [c]
NPK	0.0016	0	0.0015b [c]	0.0001	0.023	0.005	0.024	0.003
P1/2	0.0015	0.0002			0.028	0.005		
-P	0.0016	0.0005			0.025	0.006		
-P-K	0.0013	0.0001			0.02	0		
	NS [b]				NS [b]		NS [c]	
Se uptake by plant shoots (mg Se ha^{-1}) in 2010 and 2011.								
	2010				2011			
	U-A (Potato)		U-A total		U-A (Wheat)		U-A total	
	Mean [a]	SD [a]	Mean [c]	SD [c]	Mean [a]	SD [a]	Mean [c]	SD [c]
NPK	7.1	1.2	6.22	0.82	76	14	66.4a [c]	8.8
P1/2	5.4	1.3			57	13		
-P	5.7	0.3			71	0		
-P-K	6.7	0.9			61	14		
	NS [b]				NS [b]			
	Y-C (Potato)		Y-C total		Y-C (Barley)		Y-C total	
	Mean [a]	SD [a]	Mean [c]	SD [c]	Mean [a]	SD [a]	Mean [c]	SD [c]
NPK	6.6	0.1	6.26	0.33	112	25	133.9b [c]	18
P1/2	6.3	0.8			150	27		
-P	5.8	1.7			148	34		
-P-K	6.4	0.4			127	0		
	NS [b]		NS [c]		NS [b]			

[a] Values are the mean of four replications and SD is the standard deviation. [b] NS = no significant difference among four fertilizer treatments within each column. Within columns, values followed by the same letter were not significantly different (ANOVA test, $P<0.05$)

[c] Values are the mean and standard deviation of values for all fertilizer treatments and sampling depths at each field site. NS means no significant difference between the two field sites. Values followed by different letters were found to be significantly different (ANOVA; $P<0.05$).

Table 5-6. Se transfer factor (TF) [a] from soil to plant for each fertilizer treatment and field site in 2010 and 2011

U-A (Potato)		U-A (Wheat)	
NPK	0.0021	NPK	0.054
P1/2	0.002	P1/2	0.047
-P	0.0022	-P	0.047
-P-K	0.0023	-P-K	0.05
Y-C (Potato)		**Y-C (Barley)**	
NPK	0.0024	NPK	0.036
P1/2	0.0025	P1/2	0.046
-P	0.0028	-P	0.04
-P-K	0.002	-P-K	0.032

[a] TF = Concentration of Se in plants /Concentration of Se in soil.

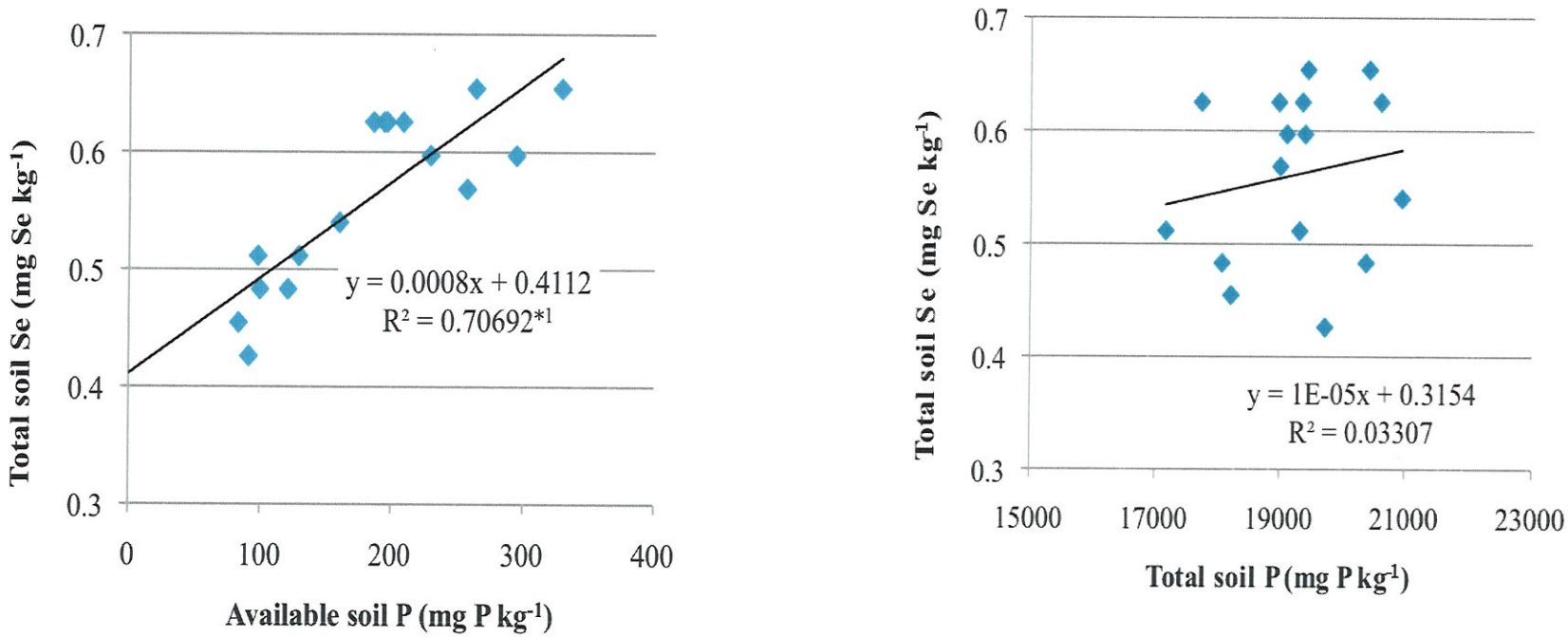


Fig. 5-1. Relationship between total soil Se and soil P. Total soil Se was found to be correlated with (a) available soil P and (b) total soil P (n=16).
[a] Statistically significant at the 0.5% level (t-test).

V.IV.IV. General discussion

V.VI.VI.I. Soil-plant transfer factor for Se at the two field sites

The increase in plant Se content associated with P fertilization may be the result of two possible mechanisms. The first mechanism is related to the input of Se along with P fertilizer. The second mechanism involves the ligand-exchangeable Se desorption from the soil as a result of P input. Nakamaru et al. (2006) reported that 18 to 70% of the Se that could be extracted from soil using 0.1 *M* Na_2HPO_4 represented ligand-exchangeable Se adsorbed to ligand-exchange sites. However, in this experiment, no increase in soil soluble Se was observed as a result of P fertilization. In order to clarify the effect of P fertilization on plant Se uptake, a soil-plant transfer factor (TF) was calculated for potato, wheat and barley shoots in 2010 and 2011 (Table 5-6). The Se TFs ranged from 0.0020 to 0.0028 for potato, 0.032 to 0.046 for barley, and 0.050 to 0.054 for wheat. No increase in TF was observed in plots receiving P fertilizer compared to plots no receiving P fertilizer, and no differences in TF were observed between the two field sites. These results suggested that P fertilization at the Y-C field site did not affect the availability of soil Se. Thus, we assume that the increase in plant Se content at the Y-C field site is primarily due to the historical accumulation of Se resulting from long-term P fertilization. From these results, we can conclude that the long-term P fertilization in Northern Japan contributes to increased Se uptake by crops and that the presence of Se is due to the inadvertent input of Se along with P fertilizer.

V.VI.VI.II. Possible fate of selenium with phosphorus fertilizer

Adequate soil phosphorus (P) is essential for optimal crop yields. However, as described in this chapter, applied P fertilizer increase Se concentration in soil. There are two possible scenarios for the fate of selenium increased in soil. The first scenario was described as follows. In many studies, interaction between two elements in the soil relative to their uptake by plant has been observed many time. When P was added to agricultural system, it replaced some Se certain adsorbed to soil minerals forcing the replaced Se react in such a way that it is more available to plants than the adsorbed form, hence the Se concentration in these plant is increased. The next scenario is added Se with P fertilizer can be adsorbed immediately to ligand-exchange cites in acid soils like our studies soils, then the soil applied with P fertilizer has low availability in acid condition. In this study Se concentration in soil increased in resulting from P addition. However, for plant Se uptake, Se uptake level was little increased with P fertilizer in my study. It seemed that the 2nd scenario was true.

VI. Summary

Phosphorus (P) fertilizer can potentially serve as a source for Se accumulation in croplands. Furthermore, it has been reported that the addition of P fertilizer to soil may enhance Se availability. Japanese agricultural soils are typically enriched in P as a result of long-term, excessive P fertilization. Therefore, we conducted a three-year field experiment in order to evaluate the effect of P fertilization on the Se content of soils and crops. Potato, wheat and barley were cultivated with and without P fertilization at two field sites in Hokkaido (northern Japan) with different levels of historical P accumulation. The first field site consisted of an Andosol soil with low available P and the second site, a Cambisol soil with high available P. The three years of continuous P fertilization over the course of the experiment did not result in a significant increase in the Se content of soils or plants. The Se content of soils and plants, however, was higher in soil samples from the Cambisol field site than from the Andosol field site, and total soil Se was significantly correlated with available soil P. Soluble soil Se and the soil-plant transfer factor for Se were not affected by P fertilization. Thus, I concluded that the higher plant Se content at the Cambisol field site was primarily due to the higher levels of accumulated Se in the soil at the site and that historical excess P fertilization typical of agricultural soils in Japan contributes to increased Se uptake by crops.

Overall discussion

My goal of this study is to answer the question that how can we make sustainable agriculture in Northern Japan and Mongolia from a point of view of soil science. As one of the answers, I proposed the recommendation for the important to fertilization for sustainable agriculture in Northern Japan. Japanese agriculture is over modern agriculture, and long-time use of chemical fertilizers at higher level resulted in the accumulation of P and K in the soils. Fertilizer is obviously important for agricultural production, but relative importance of organic fertilizer have been getting greater as compared to chemical fertilizers in Japan. Higher level of accumulated nutrients from long-term chemical fertilizer applications in Japanese Agriculture caused i) pollution from exessive due to fertilizer from soil, ii) high availability of soil P and K, iii) low or no effect of P and K fertilization. In addition, in Abashiri area in Hokkaido, about 30 Mg ha^{-1} of animal manure is commonly applied every three years and due to the manure application, input of P and K was estimated about 450kg $P_2O_5 ha^{-1}$, and 780kg K_2O ha^{-1}. The P and K input from manure application is as much as the P and K input from chemical fertilizer. Thus, the recommended fertilization in Abashiri area is i) fertilize P and K once in 3 years and ii) use of organic manure instead of chemical fertilizer of P and K. However, quantitative evaluation of the effect of P and K in manure is a remaining issue. For more detailed recommendation, accurate or appropriate estimation of nutrient availability for various kind of manure or other organic fertilizers is needed. Not only for major nutrients, the excess use of chemical fertilizers can also change the behavior of trace elements in soil and plant. Present study clearly showed the increase of soil and plant Se due to long-time fertilization of P. But it was also shown that the increase level of Se in the soil and plants was low and not in harmful level. Therefore, it could be said that the overuse of P fertilizers did not, cause result in terms of the toxicity of Se so far, instead, it could contribute to improve Se nutrition in Japanese agricultural products. This result is fortunate for Japanese farmers, but it is only one example for Se and we have to watch carefully to other trace elements such as Cd, or As, because the knowledge for trace elements in agricultural environment is still limited.

Also, the recommendation for fertilization in Mongolia for sustainable agriculture is presented as follows. In Mongolia, fertilization is seriously important for agriculture. Though Mongolian soils have relatively better soil structure than Japanese

soils because of younger history of agricultural use, however, there are potential risks of soil erosion and the consequent land degradation in the present and future. From the present study, I considered that i) to increase the crop yield, amount of soil available N should be increased, further, ii) animal manure might increase the amount of soil available N and that would be more favorable to soil productivity than chemical fertilizers applications. Therefore, use of organic manure is more recommendable than chemical fertilizer. However, annual variability in precipitation is a strong factor affecting crop yield in this region, thus, organic fertilizers should be applied with adequate irrigation. In addition, in Mongolia there are still no sufficient system to produce organic fertilizers; such system is needed for the production of adequate and comfortable composts of animal manure for conservative agricultural system.

Summary

In the world, there are many kinds of problems on fertilizer use. Overuse of fertilizer and the impact to field soil is now big problem because of the environmental pollution by fertilizer and increasing fertilization cost. For the sustainable agricultural development in Asia, appropriate use of inorganic and organic fertilizer is needed for sustainable agriculture. The objective of this study is to optimize the both of inorganic and organic fertilization systems comparing both intensive and extensive agriculture in Japan and Mongolia of Northern Asia. In Japan, due to excessive use of fertilizers, most of Japanese agricultural soil have highly accumulated available P and K. The long-term fertilization might change the status of both major and trace elements in the soil. Major elements such as P and K are certainly important for crop productivity, however, trace elements are also important for human and animal health. I focused on one trace element, selenium (Se), because P fertilizers contain Se and P addition possibly increase Se availability to plants. Se is important nutrient for animals in adequate level but it is also toxic at high concentration.

I studied the effect of long- term low or no P/K fertilization on crop productivity, and on soil and plant Se with a field experiment from 2009 to 2011. In Abashiri area, two types of fields with four plots were used; Urashibetsu (Andosol) field and Yasaka (Cambisol) field. Yasaka (Cambisol) field is older filed and has two times higher level of accumulated P than Urashibetsu (Andosol) field. In these fields, 450kg $P_2O_5 ha^{-1}$, and 780kg K_2O ha^{-1} input by animal manure application of 30 Mg ha^{-1} and 10 Mg ha^{-1} y^{-1}, respectively, was estimated. Four plots were established; i) Conventional NPK application plot, ii) half P application plot, iii) no P application plot, iv) no P, no K application plot. Tested plants were sugar beet, potato, wheat, and barley. Crop yield, Se in soil and in plant was observed. As a result, almost no significant effects of P/K fertilization on crop yield were observed during three years. Therefore, the conventional fertilization of P and K was considered to be not effective because of the accumulated P and K in the field soil. The P and K input due to manure was also regarded as important factor. For the effect of fertilizers on soil and plant Se, Se increase in soil and in plant was observed especially for Cambisol field. I concluded that the higher plant Se content at the Cambisol field site was primarily due to the higher levels of accumulated Se in the soil at the site and that historical excess P fertilization typical for agricultural soils in

Japan contributes to increase Se uptake by crops. On the other hand, fertilizer use in a developing country is also studied. Recently, the agricultural soil productivity of Mongolia have decreased by an increasing desertification and a soil erosion for no sustainable crop management. For the last 20 years, most of the farmers in Mongolia have never used any mineral fertilizers and pesticides for crop production due to insufficient supply or lack of financial resources. Thus, detailed scientific analysis of this controversial issue is needed. The possibility of animal manure use in Mongolia was tested in the field study. In this study, I used manure made from sheep and goats dung because these animals are most common livestock in Mongolia. Potato, rye, and turnip were used as test crops. In this field study, three fertilization patterns were used. i) no fertilization (control plots); ii) application of animal manure of 40 Mg $ha^{-1}y^{-1}$ (manure plot); and iii) application of chemical fertilizer of 90 kg N $ha^{-1}y^{-1}$, 90 kg P_2O_5 $ha^{-1}y^{-1}$ and 90 kg K_2O $ha^{-1}y^{-1}$ (NPK plot). As a result, applied chemical fertilizer had no effect on crop yield, and manure increased turnip yield. Also increase of soil available N was observed for manure plot. From these results, I considered that i) to increase the crop yield, amount of soil available N should be increased, further, ii) animal manure might increase the amount of soil available N and that was more favorable to soil productivity than chemical fertilizer applications. Add to this, a small field experiment was conducted to test the effect of manure amount (20-60 Mg ha^{-1}) on potato and wheat yield using long-time (2 year) matured and short-time (2mouth) matured manure. As a result, only long-time matured manure increased crop yield significantly. In this study, it was shown that long maturing time of manure and applied manure amount had positive effect on crop yield. For crop yield, recommendable use of animal manure was expected to be 20Mg ha^{-1} with matured manure in Mongolia because there was no significant difference in crop yield between 20 to 60 Mg ha^{-1} of manure application.

Key words: *Decreased fertilization, Manure, Phosphorus, Potassium, Selenium, Speciation, Excess P fertilization, Field experiment, Soil-Plant transfer, Se accumulation, Se bioavailability, Mongilia, Kastanozem, Animal manure, Crop rotation*

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Appendices 1.

OLSEN'S SODIUM BICARBONATE EXTRACTION

1. Principle of the method

1.1. The extraction is a 0.5M sodium bicarbonate ($NaHCO_3$) solution a pH of 8.5 (Olsen et., 1954). This method is suitable for Mongolian soil because most of soils in Mongolia is alkaline The solubility of calcium phosphate in calcareous, Alkaline, or neutral soils is increased because of the precipitation of calcium (Ca^{2+}) as calcium carbonate ($CaCO_3$). In acid soils, phosphorus (P) concentration in solution increases when aluminum and iron phosphate, such as variscite and strengite, are present (Lindsay and Moreno, 1960). Secondary precipitation reaction are reduced in acid and calcareous because iron (Fe), aluminum (Al), Ca concentration remain low in the extract (Olsen and Dean, 1965). Recent studies have shown that the maintenance of the pH of the extract at 8.5 is essential to obtain reliable results.

1.2. The extractant was first developed and described by Olsen et al. (1954). The original procedure required that 5g soil be shaken for 30 minutes in 100 mL extraction reagent containing 1 teaspoon of carbon black (Darco G-60). The use of carbon black eliminated the color in the extract. This procedure was later modified so that the use of carbon black was eliminated (Watanabe and Olsen, 1965). In the modified method, a single solution reagent which consists of an acidified solution of ammonium molybdate containing ascorbic acid and a small amount of antimony (Sb) is used (Murphy and Riley, 1962; Watanabe and Olsen, 1965). The method is described by Anon. (1994b) and Frank et al. (1998). Comparison between the Olsen and other methods of P extraction has been by Wolf and Baker (1989).

2. Range, Sensitivity, and Methods of Analysis

2.1. The molybdate complex obeys Beer's Law, yielding a straight line when the log of % transmittance versus concentration is plotted up to a concentration of 2 mg PL^{-1} in the final solution (Murphy and Riley, 1962).

2.2. The sensitivity of this method is 0.02 mg PL^{-1} in extract (Watanabe and Olsen, 1965).

2.3. The commonly used method of analysis is UV-VIS spectrophotometry (Waston and Lsaac, 1990; wright and Stucznski, 1996).

3. Interferences

3.1. This method provides noninterference of silicate in solution up to at least 10 mg silicon (Si) L^{-1}, up to at least 50 mg Fe (III) L^{-1}, up to at least 10mg copper [Cu(II)] L^{-1}, and up to at least 1 mg arsenate L^{-1}(Murphy and Riley, 1962).

4. Precision

4.1. The coefficient of variation (CV) depends on the concentration of P in the extract. For routine analysis, the CV may vary from 10 to 20%.

5. Apparatus

5.1. No. 10 (2-mm opening) sieve.

5.2. 2-cm^3 scoop, volumetric.

5.3. 250- mL extraction bottle or flask, with stopper.

5.4. Mechanical reciprocating shaker, 180 oscillation per minute.

5.5. Filter funnel, 11 cm.
5.6. Funnel rack.
5.7. Whatman No.40 filter paper (or equivalent), 12.5 cm.
5.8. UV-VIS spectrophotometer set at 880 nm.
5.9. Spectrophotometric tube or cuvet.
5.10. Analytical balance.
5.11. Volumetric flasks and pipettes as required for preparation of reagents, standard solutions, and color development.

6. Reagents (use reagent grade chemical and pure water)

6.1. Extraction reagent (0.5 N Sodium Bicarbonate): Dissolve 42.0g sodium bicarbonate ($NaHCO_3$) in water in a 1,000-mL volumetric flasks and bring to volume with water. Adjust the pH to 8.5 with 50% sodium hydroxide (NaOH) or 0.5N hydrochloric acid (HCI). Add mineral oil to avoid exposure to air. Store in a polyethylene container and check the pH of the solution before use and adjust if necessary (Note: maintenance of the pH at 8.5 is essential).

6.2. Mixed Reagent: weigh 12.0 g ammonium molybdate [$(NH_4)_6 Mo_7 O_{24}$ $4H_2O$] into 250 mL water, and mix to dissolve. Weight 0.2908 g antimony potassium tartrate [$K(SbO)C_4 H_4 O_6$. 1/2 H_2O] into 500mL 5N sulfuric acid ($H_2 SO_4$) (148mL conc. $H_2 SO_4$ L^{-1}), and mix to dissolve. Mix the two solutions together thoroughly in a 2,000 mL volumetric flask and bring to volume with water. Store in a pyrex bottle in a dark, cool place.

6.3. Color-Developing Reagent: Add 0.739 g ascorbic acid to 140 mL Mixed reagent (see 6.2). This amount of reagent is enough for 24 P determinations, allowing 20mL for waste. This reagent should be prepared as required as it will not keep or more than 24 hours.

6.4. Phosphorus Standard (100mg P L^{-1}): Commercially prepared standard, or weigh 0.4394 g monobasic potassium phosphate ($KH_2 PO_4$) that has been oven-dried at 110^0C into a 1,000-mL volumetric flask, add mL water to dissolve, and bring to volume with water. Add 5 drops of toluene and shake the flask vigorously. This solution contains 100 mg P mL^{-1}.

6.5. Working Phosphorus Standard: Pipette 1, 2, 5, 10, 20, and 30 mL of the 100 mg P L^{-1} phosphorus (see 6.4) into 100-mL volumetric flasks and bring to volume with Extraction Reagent (see 6.1) to give 0.1, 0.2, 0.5, 1.0, 2.0, and 3.0 mg P L^{-1} working P standards, respectively.

7. Procedure

7.1. Extraction: weigh 2.5 g or scoop 2-cm^3 (see 5.2) air-dry, <10-mesh (2-mm) soil into a 250-mL extraction bottle (see5.3), 50 mL Extraction Reagent (see 6.1), and shake for 30 minutes on a reciprocating shaker (see 5.4). Filter and collect the filtrate (Caution: Soil extraction is sensitive to temperature changing 0.43 mg P kg^{-1} for each degree C for soils containing 5 to 40 mg P kg^{-1}).

7.1. Color Development: Pipette 5 mL extract (see 7.1) and Working phosphorus Standards (see 6.5) into spectrophotometric tubes which are optically similar (see 5.9). Add 5 mL Color Development Reagent (see 6.3) carefully to prevent loss of the sample due to excessive foaming. Add 15 mL water with a burette and stir. Let it stand 15 minutes

and measure the color intensity (%T) at 880 nm. If the color is too intense for the working range, reduce the aliquot from 5 mL to a lower volume and add sufficient Extraction Reagent (see 6.1) to bring the aliquot volume to 5 mL (if 1 mL aliquot is used, 4 mL Extraction Reagent is added to the aliquot). Develop the color. The color is stable for 24 hours.

8. Calibration and Standards

8.1. Color Development of Phosphorus Standards: Pipette aliquots of dilute Working Phosphorus Standards (see 6.5) containing from 2 to 25 mg P L^{-1} (1 mL to 12.5 mL) into 25 mL volumetric flasks. Add 5mL Color Development Reagent (see 6.3) and mix. Bring to volume with the Extraction Reagent and mix thoroughly. Let stand 15 minutes and read the transmittance at 880 nm.

8.2. Calibration Curve: On semi-log graph paper the percentage of transmittance (% T) on the logarithmic scale versus mg P L^{-1} in the solution on the linear scale. Construct a table from the calibration curve showing the relationship between the % T and P concentration. Check two points on the calibration curve on every day of P analysis.

9. Calculation

9.1. The results are reported as kg P ha^{-1} for a 20-cm depth of soil: kg P ha^{-1} in the soil =mg L^{-1} in the final solution X 250. These calculations are for a 5 mL aliquot of extract and should be adjusted for other aliquots. To express the results on a soil-weight basis, use the following formula: mg P kg^{-1} in soil =mg P L^{-1} in solution X 20.

10. Effects of Storage

10.1. Air-drying and storage may have some effect on $NaHCO_3$ –extractable P. However, for routine soil testing purposes, this effect is not significant. The influence of storage time and temperature is discussed by Houba and Hovozamsky (1998).

10.2. After extraction, measure the P in the extraction within two hours.

11. Interpretation

11.1. It has been shown by several workers (Olsen and Dean, 1965) that a P content of <12 kg ha^{-1} in soil indicates a crop response to P fertilizers, between 12 and 14 kg ha^{-1} indicates a probable response, and >24 kg ha^{-1} indicates a crop response is unlikely. However, differences in climatic conditions and crop species may make the general guidelines given above not applicable to all conditions (Peck et al., 1977; Brown, 1987; Dahnke and Olsen, 1990; Withers and Sharpley, 1995).

NEURAL NORMAL AMMONIUM ACRTATE EXTRACTION (POTASSIUM, CALCIUM, MAGNISUM, And SODIUM)

1. Principle of the Method

1.1. This method uses a neutral salt solution to replace the cations present in the soil exchange complex; therefore, the cation concentrations determined by this method are referred to as "exchangeable" for non-calcareous soils. For calcareous soils, the cations are referred to as "exchangeable plus soluble."

1.2. the use of neutral normal ammonium acetate (1N $NH_4C_2H_30_2$, pH 7.0) to determine exchangeable potassium (K) was first described by Prianschnikov (1913). Schollenberger and simon (1945) describe the advantages of this extracting reagent as its effectiveness in wetting soil, replacing exchangeable cations, ease of volatility during analysis, and suitability for use with flame emission spectrophotometry. More recently, this method was described by Jakson (1958), chapman (1965), Hanlon and Jahnson (1984), Haby et al. (1990), Bates and Richards (1993), Simard (1993), Anon. (1994c), Helmeke and Sparks (1996), and Warncke and Brown (1998). The 1N NH_4C_2 H_3 O_2, pH 7.0 extraction procedure is the most commonly used extraction reagent for determining K, magnesium (Mg), calcium (Ca), and sodium (Na) in soil testing laboratories in the United State (Jones, 1973, 1998b).

2. Range, Sensitivity, and Analysis Methods

2.1. The range of detection will depend on the particular analytical instrument, a range that can be extended by diluting the extract.

2.2. sensitivity will vary with type of analytical instrument used, wavelength selected, and method of extraction.

2.3. The commonly used methods of analysis are flame emission or atomic absorption spectrometry (AAS) (Watson and Isaac, 1990; Wright and Stuczynski, 1996), or inductively coupled plasma emission spectrometry (ICP-AES) (Soltanpour et al., 1996, 1998). The use of an Auto Analyzer has been described by Isaac and Jones (1970, 1971) and Flannery and Markus (1972).

3. Interferences

3.1. Under certain conditions, Extraction Reagent (see 6.1) will extract more K, Mg, Ca, and/ or Na than is found in exchangeable from, such as those elements released by weathering action during the period of extraction, and Ca and Mg released through the dissolution of the carbonate from of these elements. The additional amounts of these elements will not usually or significantly alter an analysis for soil fertility evaluation. If the cation exchange capacity (CEC) is estimated by cation summation and the percentage of base saturation is used to assess the fertility status of the soil, then the interference is significant.

3.2. Known interferences and compensation for the changing characteristics of the extract to be analyzed must be acknowledged. The use of internal standards, such as lithium (Li) and compensating elements such as lanthanum (La), are essential in most flame methods of extraction (Watson and lsaac, 1990; Wright and Stuczynski, 1996).

4. Precision and Accuracy

4.1. Repeated analysis of the same soil with medium concentration ranges of K, Ca, Mg, and Na will produce coefficients of variations of 5 %-10%. A major portion of the variance is related to the heterogeneity of the soil rather than to the extraction or method of analysis.

4.2. The level of exchangeable K will increase upon air drying of same soils (Sparks, 1987). Soil samples can be extracted in the moist state. However, the difficulties inherent in handing and storing moist state. However, the difficulties inherent in handling and storing moist soil hinder the easy adaptation of this method to a routine method of analysis. Compensation can be made, based on the expected release of K by the particular soil being tested.

5. Apparatus

5.1. No. 10 (2-mm opening) sieve.

5.2. 4.25-cm^3 scoop, volumetric.

5.3. 50- mL extraction bottle or flask, with stopper.

5.4. Mechanical reciprocating shaker, 180 oscillation per minute.

5.5. Filter funnel, 11 cm.

5.6. Funnel rack.

5.7. Whatman No.1 filter paper (or equivalent), 11 cm.

5.8. Flame emission, atomic absorption spectrophotometer (AAS), inductively coupled plasma emission spectrophotometer (ICP-AES), or AutoAnalyzer Systems.

5.9. Analytical balance .

5.10. Volumetric flasks and pipettes as required for preparation of reagents, standard solutions.

6. Reagents (use reagent grade chemical and pure water)

6.1. Extraction Reagent: Dilute 57 mL glacial acetic acid ($HC_2H_3O_2$) with water to a volume of approximately 500 mL. then add 69mL conc. Ammonium hydroxide (NH_4OH). CAUTION: Use a fumehood. Add sufficient water to obtain a volume of 990mL. After thoroughly mixing the solution, adjust the pH to pH 7.0 using either 3 N ammonium hydroxide (NH_4OH) or 3 N $HC_2H_3O_2$. Dilute to a final volume of 1,000 mL with water.

Alternate Method: Weigh 77.1 g ammonium acetate (NH_4 $C_2H_3O_2$) in about 900 mL water in a 1,000-mL volumetric flask. After thoroughly mixing the solution, adjust the pH to 7,0 using either 3 N $HC_2H_3O_2$ or 3 N NH_4OH. Bring to volume with water.

6.2. Potassium Standard (1,000 mg K L^{-1}): Commercially prepared standard, or weigh 1.9080 g potassium chloride (KCl) into a 1,000-mL volumetric flask and bring to volume with Extraction Reagent (see 6.1). Prepare the working standards by diluting aliquots of this stock solution standard with Extraction Reagent (see 6.1) to cover the anticipated range in concentration to be found in the soil extraction filtrate. Working standards from 5 to 100 mg K L^{-1} should be sufficient for most soils.

6.3. Calcium standard (1,000 mg Ca L^{-1}): Commercially prepared standard, or weigh 2.498 g calcium carbonate ($CaCO_3$) into a 1,000-mL volumetric flask. Add 50 mL water and add dropwise a minimum volume (approximately 20mL) conc.

Hydrochloric acid (HCl) to effect the complete solution of the $CaCO_3$. Dilute to the mark with Extraction Reagent (see 6.1). Prepare the working standards by diluting aliquot of this stock solution standard with Extraction Reagent (see 6.1) to cover the anticipated range in concentration to be found in the soil extraction filtrate and to fit the working range of the instrument.

6.4. Magnesium standard (1,000 mg Mg L^{-1}): Commercially prepared standard, or weigh 1,000g magnesium (Mg) ribbon into a 1,000-mL volumetric flask and dissolve in a minimum volume of dilute HCl. Dilute to 1,000 mL with Extraction Reagent (see 6.1). Prepare the working standards by diluting aliquot of this stock solution standard with Extraction Reagent (see 6.1) to cover the anticipated range in concentration to be found in the soil extraction filtrate and to fit the working range of the instrument.

6.5. Sodium Standard (1,000 mg Na L^{-1}) Commercially prepared standard, or weigh 2,524 g sodium chloride (NaCl) into a 1,000-mL volumetric flask and bring to volume with Extraction Reagent (see 6.1). Prepare working standards by diluting aliquots of this stock standard with Extraction Reagent (see 6.1) to cover the anticipated range in concentration to be found in the soil extraction filtrate. Working standards from 1 to 10 mg Na L^{-1} should be sufficient for most soils.

7. Procedure

7.1. Extraction: Weigh 5 g or scoop 4.25 cm^3 (see 5.2) air-dry <10 mesh (2mm) soil into a 50-mL Extraction Bottle (see 5.3), add 25 mL Extraction Reagent (see 6.1), and shake for five minutes on a reciprocating shaker (5.4). Filter and collect the filtrate.

7.2. Analysis: K, Mg, Ca, and Na in the filtrate can be determined by either flame emission, AAS, ICP-AES, or by use of an Auto Analyzer (see2.3).

8. Calibration and Standards

8.1. Working Standards: Prepared as described in Section 6. If element concentrations are found outside the range of the instrument or standards, suitable dilutions should be prepared, starting with a 1:1 soil extract-to-Extraction Reagent (see 6.1) dilution. Dilution should be made so as to minimize the magnification of error introduced by diluting.

8.2. Calibration: Procedure vary with instrument techniques and type. Every precaution should be taken to use proper procedures and to follow the manufacturer's recommendations in the operation and calibration of the analytical instrument used.

9. Calculation

9.1. The results are reported as kg ha^{-1} for a 20-cm depth of soil: kg element ha^{-1} = mg L^{-1} of element in extraction filtrate X10.

9.2. To convent to other unite for comparison (see Mechlish, 1972, 1974).

10. Effect of Storage

10.1. Soil may be stored in an air-dry condition for several months with no effects no the exchangeable K, Mg, Ca, and Na content. Potassium may be released or fixed upon drying for some soils (Sparks, 1987). The influence of storage time and temperature is discussed by Houba and Novozamsky (1998).

10.2. After extraction, the filtrate containing K, Mg, Ca, and Na should not be stored for longer than 24 hours unless it is refrigerated or treated to prevent bacterial growth.

11. Interpretation

11.1. An evaluation of the analytical results for determination of fertilizer recommendations, particularly for the elements K and Mg, must based on field response data conducted under local soil-climate-crop conditions (Peck et al., 1977; Brown, 1987; Dahnke and Olsen, 1990; Haby et al., 1990; Black, 1993; Mikkelsen and Camberate, 1995; Maynard and Hochmuth, 1997; Ludwick 1998; Reid 1998).

Ammonium Bicarbonate-DTPA Extraction (Nitrate Determintion)

1. Principle Of The Method

1.1. The Extraction Reagent is 1 M ammonium Bicarbonate ($NH_4 HCO_3$) in 0.005 M DTPA adjusted to a pH of 7.6 (Soltanpour and Schwed, 1977; Soltanpour and Workman, 1979; Soltanpour, 1991). The nitrate (NO_3) is soluble in any water-based solution.

2. Range, Sensitivity, and Analysis Procedure

2.1. The range and sensitivity are the same a those for other methods of NO_3 determination.

2.2. The NO_3 concentration in the extractant is determined by Spectrometry (Watson and Isaas, 1990).

3. Interferences

3.1. The Extraction Reagent is unstable with regard to pH and must be kept under mineral oil to prevent a pH change. No interference are likely if chloride (CI) ions present are masked.

4. Precision and Accuracy

4.1. A coefficient of variability ranging from 5 to 10 % can be extracted for different determinations.

5. Apparatus

5.1. No. 10 (2-mm opening) sieve constructed from stainless steel or nalgene.

5.2. Analytical balance.

5.3. 125 - mL polyethylene conical flasks.

5.4.Eberbach reciprocating shaker (or equivalent), 180 oscillation per minute.

5.5. Whatman No.42 filter paper (or equivalent), 12.5 cm.

5.6. UV-VIS spectrophotometer set at 420 nm.

5.7. 2.5 – cm matching spectrophotometric tubes.

5.8. A pH meter readable to 0.01 pH units.

5.9. Funnel and funnel rack.

5.10. Accurate automatic diluter.

5.11. Volumetric flasks and pipettes as required for preparation of reagents, standard solutions.

6. Reagents (use reagent grade chemical and pure water)

6.1. Extraction Reagent [Ammonium Bicarbonate (AB)-DTPA]: 0.005 M DTPA (diethylenetriaminepentaacetic acid) solution is obtained by adding 9.85 g DTPA (acid from) to 4,500 mL water in a 5,000 – mL volumetric flask. Shake for five hours constantly to dissolve DTPA. Bring to 5,000 mL with water. This solution is stable with regard to pH. To 900 mL of the 0.005 M DTPA solution, add 79.06 g ammonium Bicarbonate ($NH_4 HCO_3$) gradually and stir gently with a rod to facilitate dissolution and to prevent effervescence when bicarbonate is added. The solution is diluted to 1,000 mL with the 0.005 M DTPA solution and mixed gently with a rod the pH is adjusted to 7.6 with slow agitation with a rod by adding 2 M hydrochloric acid (HCl). The AB- DTPA solution must be stored under mineral oil. Check the pH after storage and adjust it with a 2 M HCl dropwise, if necessary. The cumulative volume of HCI added should not exceed 1 mL L^{-1}

limit, after which a fresh solution should be prepared. Ideally, the extraction reagent is best made as needed.

6.2. Antimony Sulfate Solution: Weigh 0.5 antimony metal (Sb) into 80 mL conc. Sulfuric acid (H_2SO_4) and then add 20 mL water to the acid carefully to prevent splattering. Heating will facilitate the dissolution of antimony (Sb) metal in H_2SO_4. This solution is used for masking (complexing) chloride (CI) the NO_3 determination.

6.3. Chromotropic Acid Solution (CTA) [0.00137 M solution of CTA or 4,5-dihydroxy-2,7-naphthanlete-disulfonic acid, disodium salt [$(HO)_2C_{10}H_4(SO_3Na)_2$]: weigh 0.5 g CTA in 0.4 kg conc. This solution is used to develop color with NO_3.

6.4. Fisher G Carbon Black: Used to eliminate organic matter interference.

7. Procedures

7.1. Extraction Method: Weigh 10 g air-dry soil <10-mesh (2mm) into a 125-mL conical flask, add 20 mL Extraction Reagent (see 6.1), and shake on an Eberbach reciprocal shaker or an equivalent shaker for exactly 15 minutes at 180 cycles per minute with flasks kept open. The extracts are then filtered through Whatmen 42 filter paper.

7.2. Determination: Mix 5 mL soil extract (see 7.1) with one 1-mL scoop of Fisher G Garbon Black (see 6.4), shake for minutes or longer if required to decolorize the solution, and filter. Place a 0.5 mL aliquot of the decolorized soil extract, Working Standards (see 8.2) and AB-DTPA [0.00 NO_3 – N solution (see 6.1)] into 2.5-cm matching spectrometric tubes. Add 3.0 mL water to each tube using an automatic diluter. Add 2.0 mL Antimony Sulfate Solution (see 6.4) followed by 6.5 mL CTA (See 6.3) in quick succession to each tube. Mix thoroughly and cool solution in tap water for consistent results. The spectrometer is set at zero absorbance at 420nm using the 0.00 NO_3 –N solution. The color intensity (adsorbance) of soil extracts is read after two hours.

8. Standards

8.1. Primary Nitrate –N standard (1,000 $NO_3 - NL^{-1}$**):** Commercially prepared standard, or weigh 3.611 g potassium nitrate (KNO_3) into a 500-mL volumetric flask and bring to volume with water.

8.2. Working Standards: Pipette 0.25, 0.5, 1, 1.5, 2.5 mL aliquots of the Primary Nitrate – N Standard (see 8.1) into 100-mL volumetric flask and bring to volume with Extraction Reagent (see 6.1) in order to obtain a series of standards containing 2.5, 5, 10,15, and 25 mg $NO_3 - NL^{-1}$, respectively.

9. Calculations

9.1. mg NO_3 –N kg^{-1} in soil = mg $NO_3 - NL^{-1}$ in extract X 48.

10. Effect of Storage

10.1. Air-drying and storage should not have any significant effect on the level of NO_3 in the soil (Houba and Novozamsky, 1998).

10.2. The Extraction Reagent (see 6.1) must be stored under mineral oil.

11. Interpretation

11.1. Interpretation of the test results will depend on their use as described by Magdoff et al. (1948), Magdoff et al. (1990), Dahnke and Johnson (1990), Schmitt and Randall (1994), Muchovej and Rechcingl (1995).

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